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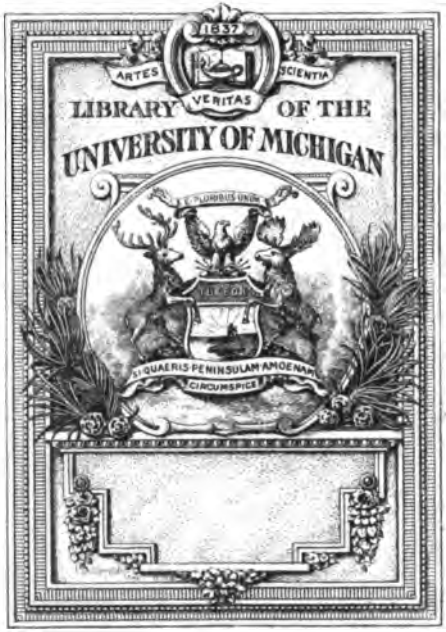

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THE

Journal of Analytical Chemistry

33885

VOL. II, 1888.

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EASTON, PA.
PUBLISHED BY THE EDITORS.

GEORGE W. WEST, BOOK AND COMMERCIAL PRINTER.
1888.

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VOL. II. [JANUARY, 1888.] PART I.

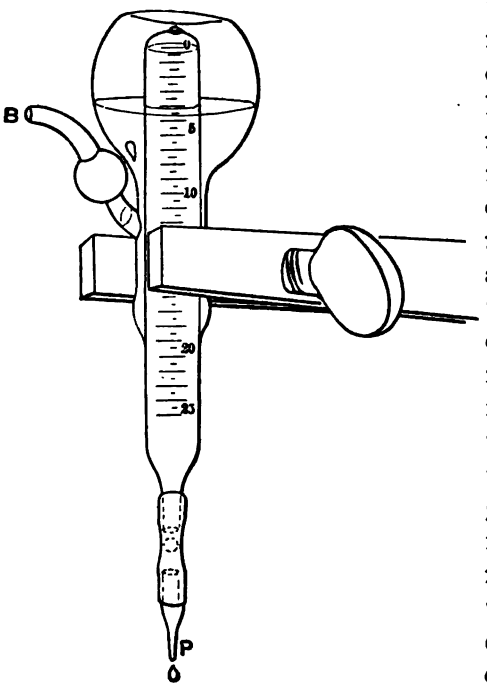
THE

Journal of Analytical Chemistry.

A BURETTE FLASK.

BY F. H. MORGAN.

THE accompanying figure represents a new form of weighing flask. It differs from all flasks intended for a similar purpose hitherto devised, in that it measures the volume of liquid used, yet being just as convenient for weighing as any of them. The operator, knowing about how much reagent will be needed, can, as with an ordinary burette, run in nearly all the reagent at once. As shown by the diagram, it consists of a short graduated burette inverted in the neck of a light flask, to the mouth of which it is joined by fusion or ground to form a tight-fitting stopper. The flask has a lateral bulbed tube, for entrance or exit of air or any gas under which it may be de-



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sired to keep the reagent. The burette reaches to within a millimeter of the bottom of the flask and has only a very small aperture for the admission of liquid from the flask.

The reagent to be used is run in at P. The burette is filled from the flask by pressure at B, the valve at P being held open until it is full. In use, the flask is inverted in a revolving clamp stand and used as an ordinary burette, air (or gas) entering at B as liquid is drawn out at P. (See fig.)

When the burette is to be refilled, the flask is brought upright and suction first applied at B, to draw the few drops of liquid remaining in the jet down into the burette; pressure being then applied at B, the burette may be filled without any loss at P.

I have used two of these burette-flasks, made for me by Emil Greiner, of New York, for nearly a year and have found them very convenient in certain kinds of work. They weigh only forty to forty-five grms., and with 50 c. c. of reagent may be weighed on an ordinary balance. In the determination of iron by direct reduction with $SnCl_2$, I have been able to use a reagent one gram of which is capable of reducing ninety mgrms. of Fe''', or about ten times the ordinary strength.

In a subsequent number I hope to publish some results obtained by the use of strong reagents in this burette-flask in a series of experiments not yet finished.

ANALYTICAL LABORATORY, CORNELL UNIVERSITY.

ELECTROLYSIS OF WATER.

BY F. P. VENABLE.

THE short note in the JOURNAL OF ANALYTICAL CHEMISTRY, No. 3, 1887, p. 287, describing a simplification of the ordinary condenser has proved of such use to me that I venture to publish this notice of a simplification of Hofmann's apparatus for the electrolysis of water which may prove useful to some teacher at a distance from chemical supply stores and placed in the awk-

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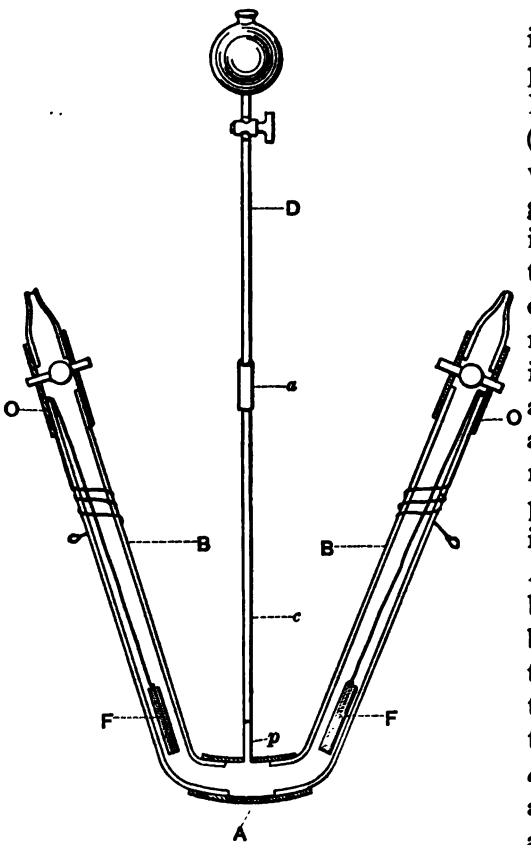
ward predicament I found myself in a short time ago. The usual piece of apparatus was broken and there was no time for ordering another so that I was forced to put together the apparatus from what was at hand in the laboratory. As it answers every purpose, working very nicely, can be put together in a short time, and costs much less than the seven or eight dollars which the original apparatus cost, I think I will rest content with it in the future instead of the more expensive shop-made article.



The accompanying figure will explain the apparatus. B B are two tubes (about 8 by ½ in.) which can easily be gotten in the form in the diagram by taking a single tube of double the length mentioned, giving it the desired bend and then scratching and breaking in the middle. A stout piece of rubber tubing unites these at A. This tubing is by means of a cork-borer perforated in the centre between the tubes B. Into this opening a tube *c* is inserted bent at right angles at *p* and with its end enlarged to prevent leaking. It is not necessary to bend at right-angles for some kinds of supports, but the opening in the rubber A may be directly on top and the tube *c* let right into it.

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D is a funnel with stop-cock fastened to *c* by the rubber connection *a*. Into the tubes B wires F F (best of platinum with flattened ends, though copper will answer) are placed, reaching nearly to the bend and coming out under the rubber connections O O, passing a short way down the outside, wound round the tube two or three times and ending in loops to which the battery wires may be attached. The tubes B B are connected with jet pieces by means of rubber tubing and can be tightly closed by pinch-cocks. All rubber connections must be tightly wound with wire to prevent leakage. The gases produced can be examined at the jets or a delivery tube attached, running under a test-tube which is placed in a pneumatic trough. As a support the ordinary iron retort stand may be used, fastening the tubes with wires. It is better however to have a board, blackened or covered with black paper, and nailed to a block so as to stand upright. The tubes B B can be fastened to this by wires going through gimlet-holes. The funnel D can rest in a hole or slit cut in a thin strip tacked across the top of the board.

UNIVERSITY OF NORTH CAROLINA, OCTOBER 1887.

COBALT SOLUTION AS AN INDICATOR IN FERRIC IRON DETERMINATIONS.

BY ALONZO C. CAMPBELL.

IN the July number of the JOURNAL OF ANALYTICAL CHEMISTRY F. P. Venable gives an account of a delicate qualitative test for ferric iron by the use of cobalt nitrate.

Believing that the delicacy of the test might be of service as an indicator in the volumetric determination of ferric chloride by means of stannous chloride, I put the matter to the test. Unguardedly, in my first experiments I used cobalt nitrate, and my results were somewhat discordant. I then prepared a solution of cobaltous chloride using an excess of strong hydrochloric acid, which latter imparted to the solution the charac-

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teristic clear blue. I will give an account of my investigations, since they may prove of some interest and be instructive in revealing other possibilities of the method and the nature of the reactions. I dissolved 5 gms. of iron wire in hydrochloric acid, peroxidized with potassium chlorate, boiled, then diluted to 500 c. c.

I prepared a solution of stannous chloride and protected it from oxidation by a cover of kerosene, using the ordinary wash-bottle attachment of mouth-piece and jet as a convenience for discharging the solution into the burette by blowing into the mouth-piece.

I used a 20 c. c. pipette to draw off that quantity of ferric chloride, which latter was introduced into a small flask of about 200 c. c. Six or eight drops of dilute cobalt nitrate were then added. The flask being then properly supported, a small flame was placed under it so that gentle ebullition was kept up. The burette filled to 0 with the tin solution was then suspended so that the jet entered the mouth of the flask.

The tin solution being allowed to run or drop into the flask during the active ebullition of the solution of iron, the deep yellow of the latter gradually and markedly changed into yellowish green, then pure green, then rapidly clearing up presented a pure blue.

The clear blue is strikingly different from the slightly turbid green which just precedes it. I repeated the operation several times and the results varied from 17 c. c. to 20 c. c. or more.

This inconstancy of results suggested that there might be some effect due to the small amount of nitric acid of the cobalt nitrate. I then made several test tube trials using the nitrate of cobalt as before and discovered that in relatively dilute solutions the blue would make its appearance, but after a few moments' boiling the green would again supplant it. Again adding the stannous chloride the blue would appear, but by further boiling and concentration the green would return, but finally by repeated additions of tin solution the blue would ap-

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pear and remain permanently even after long boiling and concentration almost to dryness.

Thinking that an oxidizing or chloridizing influence might be the cause of the green as derived from the blue I dropped a small crystal of potassium chlorate in a hot solution of blue cobalt solution; it quickly turned green. Similarly using nitric acid, the green appeared. The green of chlorate of potassa was changed to blue again by boiling, while the green of nitric acid and ferric iron is not dissipated by boiling. The nitric acid might however be destroyed by concentration and repeated additions of hydrochloric acid.

The precautions suggested by these preliminary experiments were carefully carried out and the determinate results were most satisfactory.

The 20 c. c. of ferric chloride solution evaporated nearly to dryness to expel every trace of chlorous fumes and then a few drops of cobaltous chloride added and the titrations proceeded with during active ebullition, the results were almost invariably 14.5 c. c. of tin solution, and the first appearance of the blue remained unalterable after prolonged boiling.

It is necessary to conduct these operations with deliberation and care, and to observe the precaution to keep up the ebullition unceasingly.

Since the blue cobalt solution is so sensitive to the presence of nitric acid it might be used as a qualitative test for its presence, and it might also be a means of its volumetric determination. The addition of a small proportion of ferrous iron to the solution holding the nitric acid or nitrate to be determined would act as a carrier of the oxygen or its effect in the perchloridization of the tin. A sufficient excess of ferrous iron, together with concentration, would effectually destroy the nitric acid with the liberation of N_2O_2 and thus impart its full oxidizing effect to the iron.

It is further evident that any oxidizing or perchloridizing agent may be similarly determined or estimated volumetrically provided always that the full effect of the agent may be imparted to the iron or stannous chloride.

MINERALOGICAL LABORATORY OF VANDERBILT UNIVERSITY, NASHVILLE, TENN.

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ANALYSES OF NORTH CAROLINA WINES.

By F. P. Venable and W. B. Phillips.

So far as we are aware no analyses of the wines produced in this State have ever been published. As the industry has grown greatly in the past few years and gives promise of still greater growth, it is manifestly of importance that these wines should be analyzed. A comparison is thus possible with the wines of other localities and our knowledge of the chemistry of wines increased. The wines were in all save one case furnished us direct by the makers. Where we learned of additions made to the fermented juice of the grape, at least so far as sugar is concerned, due mention is made of it.

Of special interest are the analyses of wines made from the native scuppernong vine and the closely related vines—the Mish or Meish and Bulay. The scuppernong is very abundant, hardy and prolific in certain sections of the State, and the problem of fermenting and blending so as to secure a good wine from it is very important.

The methods of analysis recommended by the German Commission of 1884, as recorded by Barth, were used in the main. With regard to the volatile or acetic acid, the total acid was first determined then that which was left after evaporation on the water-bath. This evaporation was repeated one or more times with fresh water before the second titration. The method was carefully tested and found to be correct. The tannin was determined by comparison of the depth of precipitate produced by ferric chloride after the addition of sodium acetate, with that produced in solutions containing known amounts of tannin. The extract was determined by evaporation on a water-bath followed by 2½ hours heating in the steam-bath. As the temperature of the steam-bath generally lies between 95° and 97°, the results thus obtained are high compared with those gotten by heating at 100° or 110°.

The tables are appended.

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Variety of Wine.	*Maker.*	*Vintage*	*Specific Gravity*	*Alcohol by wight*	*Alcohol by volume*	*Acid Tartaric*	*Acid Acetic*	*Total Acid*	*Sugar*	*Tannin*	*Extract*	*Ash*
Dry Mish	C. W. Garret & Co.	1885	.9957	9.51	11.81	.655	.044	.699	.60	.020	3 162	.122
Dry Bulay	" "	1885	.9951	8.38	10 40	.818	.031	.849	.45	.015	2.179	.113
Dry Impe'l Scuppernong	" "	1885	1.0009	9.37	11.62	.770	022	.792	2 20	.025	4.259	.106
Dry Impe'l Scuppernong	" "	1884	.9949	9 36	11.61	.713	.055	.765	.08	.025	2 597	.110
Dry Mish	" "	1884	.9946	9.64	11.96	.568	.041	.609	.31	.025	2.459	.128
Dry Black Scuppernong	" "	1886	.9944	8.43	10.47	.655	.026	.681	20	.030	2.335	.139
Dry Norton	" "	1885	.9965	9.14	11.35	.724	.041	.765	.25	.025	2.785	.224
Scuppernong (sweet)	" "	1884	1 0323	9 07	11 26	.647	.015	.662	5.75	.020	13.889	.112
Mish (sweet)	" "	1885	1.0336	9.71	12.15	.501	.028	.529	5.50	025	14.275	.108
Norton (sweet)	" "	1885	1.0331	9.07	11.26	.693	.013	.706	4.75	.020	14.927	.197
King Grape (sweet)	N. W. Craft	1885	.9932	12.77	15.77	.770	—	.770	1.75	trace	3 320	.173
White Victory (sweet)	" "	1885	1 0392	12.38	15.30	.755	—	.755	4.25	trace	16 646	.106
Martha (sweet)	" "	1884	1 0332	11.15	13 81	.708	—	.708	2.95	.005	15.103	.148
Concord (sweet)	" "	1884	1.0317	10 85	13.43	.578	—	.578	3.00	.010	15.448	.204
*Thomasberger	H. Mahler		1.0365	11 54	14 27	.554	—	.554	3.00	.010	14 931	.090
Ives Seedling	" "	1884	.9952	10 46	12.96	.963	—	.963	.25	.030	3 137	.174
Clinton (sweet)	" "	1885	1.0314	12 92	15.96	.886	—	.886	2.00	trace	10 952	.202
Dry Scuppernong	G. W. Lawrence	1885	.9931	13 80	17 02	.655	.014	.669	.50	.005	3 698	.116
Scuppernong (sweet)	" "	1884	1.0347	11.85	14 65	.809	—	.8 9	3 00	.005	14.300	1 40

* The Thomasberger was purchased from a retail establishment and its vintage is unknown.

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OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887-'88.

METHODS FOR DETERMINING PHOSPHORIC ACID AND MOISTURE

(1) *Preparation of sample.*—The sample should be well intermixed and properly prepared, so that separate portions shall accurately represent the substance under examination, without loss or gain of moisture.

(2) *Determination of moisture.*—(*a*) In potash salts, nitrate of soda and sulphate of ammonia, heat 1 to 5 grams at 130° C. till the weight is constant, and reckon water from the loss. (*b*) In all other fertilizers heat 2 grams, or if the sample is too coarse to secure uniform lots of 2 grams each, 5 grams, for five hours at 100° in a steam bath.

(3) *Water-soluble phosphoric acid.*—Bring 2 grams on a filter, add a little water, let it run out before adding more water, and repeat this treatment cautiously until no phosphate is likely to precipitate in the filter. If the washings show turbidity after passing the filter clear up with acid. When the substance is nearly washed in this manner it is transferred to a mortar and rubbed with a rubber-tipped pestle to a homogeneous paste (but not further pulverized), then returned to the filter and washed with water until the filtrate measures not less than 250 c. c. Mix the washings. Take an aliquot portion (usually corresponding to ⅓ or ½ gram of the substance) and determine phosphoric acid, as under total phosphoric acid.

(4) *Citrate-insoluble phosphoric acid.*—Wash the residue of the treatment with water into a 200 c. c. flask with 100 c. c. of strictly neutral ammonium citrate solution of 1.09 density, prepared as hereafter directed. Cork the flask securely and place it in a water bath, the water of which stands at 65° C. (The water bath should be of such a size that the introduction of the cold flask or flasks shall not cause a reduction of the

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temperature of the bath of more than 2° C.) Raising the temperature as rapidly as practicable to 65° C., which is subsequently maintained, digest with frequent shakings for thirty minutes from the instant of insertion, filter the warm solution quickly (best with filter-pump), and wash with water of ordinary temperature. Transfer the filter and its contents to a capsule, ignite until the organic matter is destroyed, treat with 10 to 15 c. c. of concentrated hydrochloric or nitric acid, digest over a low flame until the phosphate is dissolved, dilute to 200 c. c., mix, pass through a dry filter, take an aliquot portion and determine phosphoric acid as under total.

In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated goods, it is to be made by treating 2 grams of the phosphatic material, without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, etc.) the residue insoluble in ammonium citrate is to be treated by one of the processes described below.

(5) *Total phosphoric acid.*—Weigh 2 grams and treat by one of the following methods: (1) Evaporation with 5 c. c. magnesium nitrate, ignition, and solution in acid. (2) Solution in 30 c. c. concentrated nitric acid with a small quantity of hydrochloric acid. (3) Add 30 c. c. concentrated hydrochloric acid, heat, and add cautiously and in small quantities at a time about 0.5 gram of finely pulverized potassium chlorate.

Boil gently until all phosphates are dissolved and all organic matter destroyed; dilute to 200 c. c.; mix and pass through a dry filter; take 50 c. c. of filtrate; neutralize with ammonia (in case hydrochloric acid has been used as a solvent add about 15 grams dry ammonium nitrate or its equivalent). To the hot solutions for every decigram of P_2O_5 that is present, add 50 c. c. of molybdic solution. Digest at about 65° C. for one hour, filter, and wash with ammonium nitrate solution. (Test the filtrate by renewed digestion and addition of more molybdic solution.) Dissolve the precipitate on the filter with ammonia and hot water and wash into a beaker to a bulk of not more than 100 c. c. Nearly neutralize with hydrochloric acid, cool,

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and add magnesia mixture from a burette; add slowly (one drop per second), stirring vigorously. After fifteen minutes add 30 c. c. of ammonia solution of density 0.96. Let stand several hours (two hours is usually enough). Filter, wash with dilute ammonia, ignite intensely for ten minutes, and weigh.

(6) *Citrate-soluble phosphoric acid.* The sum of the water-soluble and critic-insoluble subtracted from the total gives the citrate-soluble.

PREPARATION OF REAGENTS.

(1) *To prepare ammonium citrate solution.*—Mix 370 grams of commercial citric acid with 1,500 c. c. of water; nearly neutralize with crushed commercial carbonate of ammonia, heat to expel the carbonic acid, cool, add ammonia until exactly neutral (testing by saturated alcoholic solution of coralline) and bring to volume of two liters. Test the specific gravity, which should be 1.09 at 20° C., before using.

(2) *To prepare molybdic solution.*—Dissolve 100 grams of molybdic acid in 400 grams or 470 c. c. of ammonia of specific gravity 0.96, and pour the solution thus obtained into 1,500 grams or 1,250 c. c. of nitric acid of specific gravity 1.20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phospho-molybdate. Decant the solution from any sediment, and preserve in glass-stoppered vessels.

(3) *To prepare ammonium nitrate solution.*—Dissolve 200 grams of commercial ammonium nitrate in water and bring to a volume of two liters.

(4) *To prepare magnesia mixture.*—Dissolve 22 grams of recently ignited calcined magnesia in dilute hydrochloric acid, avoiding excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina, and phosphoric acid, filter, add 280 grams of ammonium chloride, 700 c. c. of ammonia of specific gravity 0.96, and water enough to make the volume of two liters. Instead of the solution of 22 grams of calcined magnesia 110 grams of crystallized magnesium chloride ($MgCl_2,6H_2O$) may be used.

(5) *Dilute ammonia for washing.*—One volume ammonia of

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specific gravity 0.96 mixed with three volumes of water, or usually one volume of concentrated ammonia with six volumes of water.

(6) *Nitrate of Magnesia.*—Dissolve 320 grams of calcined magnesia in nitric acid, avoiding an excess of the latter; then add a little calcined magnesia in excess, boil; filter from excess of magnesia, ferric oxide, etc., and bring to volume of two liters.

METHODS OF DETERMINING POTASH.

METHOD OF LINDO AS MODIFIED BY GLADDING.

(1) *Superphosphates.*—Boil 10 grams of the fertilizer with 300 c. c. of water for ten minutes. Cool the solution; add ammonia in slight excess, thus precipitating all phosphate of lime, oxide of iron, and alumina, etc., make up to 500 c. c., mix thoroughly and filter through a dry filter; take 50 c. c. corresponding to 1 gram, evaporate nearly to dryness, add 1 c. c. of dilute H_2SO_4 (1 to 1), and evaporate to dryness and ignite to whiteness. As all the potash is in form of sulphate, no loss need be apprehended by votalization of potash, and a full red heat must be used until the residue is perfectly white. This residue is dissolved in hot water plus a few drops of HCl; 5 c. c. of a solution of pure NaCl (containing 20 grams NaCl to the liter) and an excess of platinum solution (4 c. c.) are now added, and the whole evaporated as usual. The precipitate is washed thoroughly with alcohol by decantation and on filter, as usual. The washing should be continued even after the filtrate is colorless. Ten c. c. of the NH_4Cl solution prepared as above are now run through the filter. These 10 c. c. will contain the bulk of the impurities, and are thrown away. A fresh portion of 10 c. c. NH_4Cl is now run through the filter several times (five or six). The filter is then washed thoroughly with pure alcohol, dried, and weighed as usual. The platinum solution used contains 1 gram metallic platinum in every 10 c. c.

(2) *Muriates of potash.*—In the analysis of these salts an aliquot portion, containing .500 gram is evaporated with 10

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c. c. platinum solution plus a few drops of HCl, and washed as before.

(3) *Sulphate of potash, kainite, &c.*—In the analysis of these salts an aliquot portion containing .500 gram is taken, .250 gram of NaCl added, plus a few drops of HCl, and the whole evaporated with 15 c. c. platinum solution. In this case special care must be taken, in the washing with alcohol, to remove all the double chloride of platinum and sodium. The washing should be continued for some time after the filtrate is colorless. Twenty-five cubic centimetes of the NH_4Cl solution are employed, instead of 10 c. c., and the 25 c. c. poured through at least six times to remove all sulphates and chlorides. Wash finally with alcohol, dry, and weigh as usual.

To prepare the washing solution of NH_4Cl, place in a bottle 500 c. c. H_2O, 100 grams of NH_4Cl; shake till dissolved. Now pulverize 5 or 10 grams of K_2PtCl_6, put in the bottle, and shake at intervals for six or eight hours; let settle over night; then filter off liquid into a second bottle. The first bottle is then ready for a preparation of a fresh supply when needed.

ALTERNATE METHOD.

Pulverize the fertilizer (200 or 300 grams) in a mortar; take 10 grams, boil for ten minutes with 200 c. c. water, and after cooling, and without filtering, make up to 1,000 c. c., and filter through a dry paper. In this method, in case the potash is contained in organic compounds, like tobacco stems, cotton-seed hulls, etc., the substance is to be saturated with strong sulphuric acid and ignited in a muffle to destroy organic matter. If the sample have 10 to 15 per cent K_2O (kainite), take 50 c. c. of the filtrate; if from 2 to 3 per cent. K_2O (ordinary potash fertilizers), take 100 c. c. of the filtrate. In each case make the volume up to 150 c. c., heat to 100°, and add, drop by drop, with constant stirring, slight excess of barium chloride; without filtering, in the same manner, add barium hydrate in slight excess. Heat, filter, and wash until precipitate is free of chlorides. Add to filtrate 1 c. c. strong ammonium hydrate, and then a saturated solution of ammonium carbon-

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ate until excess of barium is precipitated. Heat. Add now, in fine powder, 0.5 gram pure oxalic acid or 0.75 gram ammonium oxalate. Filter, wash free of chlorides, evaporate filtrate to dryness in a platinum dish, and, holding dish with crucible tongs, ignite carefully over the free flame below red heat until all volatile matter is driven off.

The residue is now digested with hot water, filtered through a small filter, and washed with successive small portions of water until the filtrate amounts to 30 c. c. or more. To this filtrate, after adding two drops of strong hydrochloric acid, is added, in a porcelain dish, 5 to 10 c. c. of a solution of 10 grams of platinic chloride in 100 c. c. of water. The mixture is now evaporated on the water-bath to a thick syrup, or further treated with strong alcohol, washed by decantation, collected in a Gooch crucible or other form of filter, washed with strong alcohol, afterwards with 5 c. c. ether, dried for thirty minutes at 100° C., and weighed.

It is desirable, if there is an appearance of white foreign matter in the double salt, that it should be washed, according to the previous method, with 10 c. c. of the half-concentrated solution of NH_4Cl, which has been saturated by shaking with K_2PtCl_6, as recommended by Gladding.

The use of the factor 0.356 for converting K_2PtCl_6 to KCl and 0.19308 for converting to K_2O is continued.

METHODS FOR THE DETERMINATION OF NITROGEN.

THE ABSOLUTE OR CUPRIC OXIDE METHOD.

The apparatus and reagents needed are as follows :

APPARATUS.

Combustion tube of best hard Bohemian glass, about 26 inches long and one half inch internal diameter.

Azotometer of at least 100 cubic centimeters capacity, accurately calibrated.

Sprengel mercury air pump.

Small paper scoop, easily made from stiff writing-paper.

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REAGENTS.

Cupric oxide (coarse).—Wire form ; to be ignited and cooled before using.

Fine cupric oxide.—Prepared by pounding ordinary cupric oxide in mortar.

Metallic copper.—Granulated copper or fine copper gauze reduced and cooled in stream of hydrogen.

Sodium bicarbonate.—Free from organic matter.

Caustic potash solution.—Dissolve commercial stick potash in less than its weight of water so that crystals are deposited on cooling. When absorption of carbonic acid ceases to be prompt solution must be discarded.

LOADING TUBE.

Of ordinary commercial fertilizers take 1 to 2 grams for analysis. In the case of highly nitrogenous substances the amount to be taken must be regulated by the amount of nitrogen estimated to be present. Fill tube as follows : (1) About 2 inches of coarse cupric oxide. (2) Place on the small paper scoop enough of the fine cupric oxide to fill, after having been mixed with the substance to be analyzed, about 4 inches of the tube ; pour on this the substance, rinsing watch glass with a little of the fine oxide and mix thoroughly with spatula ; pour into tube, rinsing the scoop with a little fine oxide. (3) About 12 inches of coarse cupric oxide. (4) About 3 inches of metallic copper. (5) About 2½ inches of coarse cupric oxide (anterior layer). (6) Small plug of asbestos. (7) Eight-tenths to 1 gram of sodium bicarbonate. (8) Large, loose plug of asbestos ; place tube in furnace, leaving about 1 inch of it projecting ; connect with pump by rubber stopper smeared with glycerine, taking care to make connection perfectly tight.

OPERATION.

Exhaust air from tube by means of pump. When a vacuum has been obtained, allow flow of mercury to continue, light gas under that part of tube containing metallic copper, anterior layer of cupric oxide (see 5th above) and bicarbonate of

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soda. As soon as vacuum is destroyed and apparatus filled with carbonic acid gas, shut off the flow of mercury and at once introduce the delivery tube of the pump into the receiving arm of the azotometer and just below the surface of the mercury seal of the azotometer, so that the escaping bubbles will pass into the air and not into the azotometer, thus avoiding the useless saturation of the caustic potash solution.

When the flow of carbonic acid has very nearly or completely ceased, pass the delivery tube down into the receiving arm, so that the bubbles will escape into the azotometer. Light the jets under the 12-inch layer of oxide, heat gently for a few moments to drive out any moisture that may be present, and bring to red heat. Heat gradually mixture of substance and oxide, lighting one jet at a time. Avoid too rapid evolution of bubbles, which should be allowed to escape at a rate of about one per second or a little faster.

When the jets under mixture have all been turned on, light jets under layer of oxide at end of tube. When evolution of gas has ceased turn out all the lights except those under the metallic copper and anterior layer of oxide, and allow to cool for a few moments. Exhaust with pump and remove azotometer before flow of mercury is stopped. Break connection of tube with pump, stop flow of mercury and extinguish lights. Allow azotometer to stand for at least an hour or cool with stream of water until permanent volume and temperature are reached.

Adjust accurately the level of the KOH solution in bulb to that in azotometer, note volume of gas, temperature, and height of barometer; make calculations as usual. The labor of calculation may be much diminished by the use of the tables prepared by Messrs. Battle and Dancy, of the North Carolina Experiment Station (Raleigh, N. C.).

The above details are, with some modifications, those given in the report of the Connecticut Station for 1879 (p. 124), which may be consulted for details of apparatus, should such details be desired.

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DETERMINATION BY THE METHOD OF KJELDAHL.

REAGENTS AND APPARATUS.

(1) Hydrochloric acid whose absolute strength has been determined, (a) by precipitating with silver nitrate and weighing the silver chloride, (b) by sodium carbonate, as described in Fresenius's Quantitative Analysis, second American edition, page 680, and (c) by determining the amount neutralized by the distillate from a weighed quantity of pure ammonium chloride boiled with an excess of sodium hydrate.

(2) Standard ammonia whose strength, relative to the acid, has been accurately determined.

(3) "C. P." sulphuric acid, specific gravity 1.83, free from nitrates and also from ammonium sulphate, which is sometimes added in the process of manufacture to destroy oxides of nitrogen.

(4) Mercuric oxide, HgO, prepared in the wet way. That prepared from mercury nitrate cannot safely be used.

(5) Potassium permanganate tolerably finely pulverized.

(6) Granulated zinc.

(7) A solution of 40 grams of commercial potassium sulphide in one liter of water.

(8) A saturated solution of sodium hydrate free from nitrates, which are sometimes added in the process of manufacture to destroy organic matter and improve the color of the product. That of the Greenbank Alkali Company is of good quality.

(9) Solution of cochineal prepared according to Fresenius's Quantitative Analysis, second American edition, page 679.

(10) Burettes should be calibrated in all cases by the user.

(11) Digestion flasks of hard, moderately thick, well-annealed glass. These flasks are about 9 inches long, with a round, pear-shaped bottom, having a maximum diameter of 2½ inches, and tapering out gradually in a long neck, which is three-fourths of an inch in diameter at the narrowest part, and flared a little at the edge. The total capacity is 225 to 250 c. c.

(12) Distillation flasks of ordinary shape, 550 c. c. capacity, and fitted with a rubber stopper and a bulb tube above to pre-

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vent the possibility of sodium hydrate being carried over mechanically during distillation. This is adjusted to the tube of the condenser by a rubber tube.

(13) A condenser. Several forms have been described, no one of which is equally convenient for all laboratories. The essential thing is that the tube which carries the steam to be condensed shall be of block tin. All kinds of glass are decomposed by steam and ammonia vapor, and will give up alkali enough to impair accuracy. (See Kreussler and Henzold, Ber. Berichte, XVII, 34.) The condenser in use in the laboratory of the Connecticut Experiment Station, devised by Professor Johnson, consists of a copper tank supported by a wooden frame, so that its bottom is 11 inches above the work-bench on which it stands. This tank is 16 inches high, 32 inches long, and 3 inches wide from front to back, widening above to 6 inches. It is provided with a water-supply tube which goes to the bottom and a larger overflow pipe above. The block tin condensing tubes, whose external diameter is ⅜ of an inch, seven in number, enter the tank through holes in the front side of it near the top, above the level of the overflow, and pass down perpendicularly through the tank and out through rubber stoppers tightly fitted into holes in the bottom. They project about 1½ inches below the bottom of the tank, and are connected by short rubber tubes with glass bulb tubes of the usual shape, which dip into glass precipitating beakers. These beakers are 6½ inches high, 3 inches in diameter below, somewhat narrower above, and of about 500 c. c. capacity. The titration can be made directly in them. The seven distillation flasks are supported on a sheet-iron shelf attached to the wooden frame that supports the tank in front of the latter. Where each flask is to stand a circular hole is cut, with three projecting lips, which support the wire gauze under the flask, and three other lips which hold the flask in place and prevent its moving laterally out of place while distillation is going on. Below this sheet-iron shelf is a metal tube carrying seven Bunsen burners, each with a stop-cock like those of a gas-combustion furnace. These burners are of larger diameter at the top,

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which prevents smoking when covered with fine gauze, to prevent the flame from striking back.

(14) The stand for holding the digestion flasks consists of a pan of sheet-iron 29 inches long by 8 inches wide, on the front of which is fastened a shelf of sheet-iron as long as the pan, 5 inches wide and 4 inches high. In this are cut six holes 1⅝ inches in diameter. At the back of the pan is a stout wire running lengthwise of the stand, 8 inches high, with a bend or depression opposite each hole in the shelf. The digestion flask rests with its lower part over a hole in the shelf and its neck in one of the depressions in the wire frame, which holds it securely in position. Heat is supplied by low Bunsen burners below the shelf. With a little care the naked flame can be applied directly to the flask without danger.

THE DETERMINATION.

One gram of the substance to be analyzed is brought into a digestion flask with approximately 0.7 gram of mercuric oxide and 20 c. c. of sulphuric acid. The flask is placed on the frame above described in an inclined position and heated below the boiling point of the acid for from 5 to 15 minutes, or until frothing has ceased. The heat is then raised till the acid boils briskly. No further attention is required till the contents of the flask have become a clear liquid, which is colorless, or at least has only a very pale straw color. The flask is then removed from the frame, held upright, and, while still hot, potassium permanganate is dropped in carefully and in small quantity at a time till after shaking the liquid remains of a green or purple color. After cooling, the contents of the flask are transferred to the distilling flask with water, and to this 25 c. c. of potassium sulphide solution are added, 50 c. c. of the soda solution, or sufficient to make the reaction strongly alkaline, and a few pieces of granulated zinc. The flask is at once connected with the condenser and the contents of the flask are distilled till all ammonia has passed over into the standard acid contained in the precipitating flask previously described and the concentrated solution can no longer be

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safely boiled. This operation usually requires from 20 to 40 minutes. The distillate is then titrated with standard ammonia.

The use of mercuric oxide in this operation greatly shortens the time necessary for digestion, which is rarely over an hour and a half in the case of substances most difficult to oxidize and is more commonly less than an hour. In most cases the use of potassium permanganate is quite unnecessary, but it is believed that in exceptional cases it is required for complete oxidation, and in view of the uncertainty it is always used. Potassium sulphide removes all mercury from solution and so prevents the formation of mercuro-ammonium compounds which are not completely decomposed by soda solution. The addition of zinc gives rise to an evolution of hydrogen and prevents violent bumping. Previous to use the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates that are present which might otherwise escape notice.

The following modification must be used for the determination of nitrogen in substances which contain nitrates when it is desired to use this method.

DETERMINATION OF NITROGEN, INCLUDING THE NITROGEN OF NITRATES, BY A MODIFIED METHOD OF KJELDAHL.*

Bring from 0.7 to 1.4 grams of the substance to be analyzed into a Kjeldahl digesting flask, add to this 30 c. c. of sulphuric acid containing 2 grams of salicylic acid, and shake thoroughly. Then add *gradually* three grams of zinc-dust, shaking the contents of the flask at the same time. Finally, add two or three drops of platinic chloride solution and place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger from frothing has passed. The heat is then raised until the acid boils briskly, and the boiling continued until white fumes no longer pour out of the flask. This requires about five or ten minutes. Add now approximately 0.7 gram mercuric oxide and continue the boiling until the liquid in the flask is color-

* Described by Prof. M. A. Scovell.

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less, or nearly so. (In case the contents of the flask are likely to become solid before this point is reached add 10 c. c. more of sulphuric acid.) Complete the oxidation with a little permanganate of potash in the usual way, and proceed with the distillation as described in the method above.

DETERMINATION BY THE RUFFLE METHOD.

PREPARATION OF REAGENTS.

(1) *A standard solution of sulphuric acid*, half normal, or 19.968 grams SO_3 per liter.

(2) *A standard solution of potassium hydrate*, half normal, or 27.991 grams KOH per liter.

(3) *An alcoholic solution of cochineal.*

(4) *Hyposulphite mixture.*—Prepared by mixing equal parts by weight of soda-lime and finely powdered crystallized sodium hyposulphite.

(5) *Sugar and sulphur mixture.*—This is prepared by mixing equal parts by weight of finely powdered granulated sugar and flowers of sulphur.

(6) *Ordinary granulated soda-lime.*

APPARATUS.

(1) *Combustion tubes* of hard Bohemian glass, twenty inches long and one-half inch internal diameter, drawn to a point.

(2) *Three-bulb, 6 inch U tubes*, with glass stop-cock.

(3) *Aspirator.*

PREPARATION.

(1) Clean and fill the U tube with 10 cubic centimeters of standard acid.

(2) Fit cork and glass connecting tube. Fill the tube as follows: (1) A loosely fitting plug of asbestos, previously ignited, and then 1 to 1½ inches of the hyposulphite mixture. (2) The weighed portion of the substance to be analyzed is intimately mixed with from 5 to 10 grams of the sugar and sulphur mixture. (3) Pour on a piece of glazed paper, or porcelain mortar, a sufficient quantity of the hyposulphite mixture to fill about 10 inches of the tube; then add the substance to be analyzed, as previously prepared; mix carefully

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and pour into the tube; shake down the contents of the tube, rinse off the paper or mortar with a small quantity of the hyposulphite mixture and pour into the tube; then fill up with soda-lime to within 2 inches of the end of the tube. (4) Place another plug of ignited asbestos at the end of the tube, and close with a cork. (5) Hold the tube in a horizontal position, and tap on the table until there is a gas channel all along the top of the tube. Make connection with the U tube containing the acid, aspirate, and see that the apparatus is tight.

The combustion.—Place the prepared combustion tube in the furnace, letting the open end project a little so as not to burn the cork. Commence by heating the soda-lime portion until it is brought to a full red heat. Then turn up slowly jet after jet toward the outer end of the tube, so that the bubbles come off two or three a second. When the whole tube is red hot and the evolution of the gas has ceased and the liquid in the U tube begins to recede towards the furnace, attach the aspirator to the other limb of the U tube, break off the end of the tube, and draw a current of air through for a few minutes. Detach the U tube and wash the contents into a beaker or porcelain basin, add a few drops of the cochineal solution, and titrate.

DETERMINATION BY THE SODA LIME METHOD.

Select a tube of hard glass 14 to 16 inches long, draw one end of it to a fine point, and to the other end fit a cork, through which is passed a tube bent at right angles, the other end of which passes through a cork closing tightly one arm of a 6-inch three-bulbed U tube with glass stop-cock. Into the combustion tube first slip a loosely fitting plug of asbestos previously ignited, and then 1½ to 2 inches of soda-lime. Weigh out from 0.7 to 2.8 grams of the substance to be analyzed, and mix it on a piece of glazed paper or porcelain mortar with some finely pulverized soda-lime, and introduce the mixture into the combustion tube. The paper or mortar is then rinsed out with a small quantity of soda-lime and poured into the tube. The tube is then filled up to within 1 to 2 inches of the open end with granulated soda-lime, then with a plug of ignited

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asbestos. A free passage is formed for the evolved gases by holding the tube in a horizontal position and tapping gently on the table. Introduce the prepared combustion tube into the furnace, letting the open end project a little so as not to burn the cork, supporting the U tube by a clamp. The tube is then gradually heated, commencing at the fore part, nearest the cork, and progressing slowly towards the tail. The combustion should be conducted so as to obtain a steady and uninterrupted flow of gas. When properly carried out the acid in the U tube is never colored. When the acid begins to recede attach the aspirator to the other limb of the U tube, and start it slowly, then break off the point of the combustion tube and draw a current of air through the apparatus for a few minutes, in order to sweep all the ammonia into the acid.

Detach the U tube and wash the contents into a beaker or porcelain basin, add a few drops of an alcoholic solution of cochineal, and titrate.

The standard acid and alkali to be the same as that used in the Ruffle method.

METHOD FOR THE ANALYSIS OF CATTLE FOOD.

Hygroscopic moisture.—Dry 2 to 3 grams at 100° C. to constant weight.

Ash.—Char the substance at a low red heat, exhaust the charred mass with water, burn the insoluble residue, add the ash to the residue from the evaporation of the aqueous extract obtained above, dry the whole at 110°, and weigh. Determine carbonic acid and insoluble matter (sand and charcoal) in the product for the estimation of the pure ash.

Ether extract.—Pulverize the air-dry substance till all of it will pass through a sieve with not less than 1–60 inch mesh; dry about 5 grams at 100°, and take about 2 grams for each extraction. Exhaust with anhydrous ether of specific gravity .720–.725, not less than eight hours continuously. Dry ether extract at 100° in a current of dry hydrogen to a constant weight.

Crude protein.—Determine nitrogen by the Kjeldahl method

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in the manner recommended by the Nitrogen Committee, and multiply the result by 6.25 for the crude protein.

Albuminoid nitrogen, Stutzer's method.— Prepare cupric hydrate as follows : Dissolve 100 grams of pure cupric sulphate in 5 liters of water, and add 2.5 c. c. of glycerine ; add dilute solution of sodium hydrate till the liquid is alkaline, filter, rub the precipitate up with water containing 5 c. c. of glycerine per liter, and then wash by decantation or filtration till the washings are no longer alkaline. Then rub the precipitate up again in a mortar with water containing 10 per cent. of glycerine, thus preparing a uniform gelatinous mass that can be measured out with a pipette. Determine the quantity of cupric hydrate per 1 c. c. of this mixture.

To 1 gram of the substance, pulverized as for the determination of the ether extract, add 100 c. c. of water in a beaker, heat to boiling, or in case of substances rich in starch heat on the water bath ten minutes, add a quantity of the cupric hydrate mixture containing 0.7 to 0.8 grams of the hydrate, stir thoroughly, filter when cold, wash with cold water, and without drying put the filter and its contents into the concentrated sulphuric acid for the determination of the nitrogen after Kjeldahl. For filtering use either Schleicher and Shull's No. 589 filter paper or Swedish paper, either of which contains so little nitrogen that it can be left out of account.

If the substance examined consists of seed of any kind or residues of seeds, such as oil cake or anything rich in alkaline phosphate, add a few cubic centimeters of a concentrated solution of alum just before adding the cupric hydrate, and mix well by stirring. This serves to decompose the alkaline phosphate, precipitating aluminum phosphate ; if this is not done cupric phosphate and pure alkali may be formed, and the protein copper may be partially dissolved in this alkaline liquid.

Crude fiber, Weende method.—Pulverize as for the ether extract, and extract the fat, at least nearly completely. To 2 grams of the substance in an Erlenmeyer flask add 200 c. c. of boiling 1.25 per cent. sulphuric acid, boil immediately and for thirty minutes continuously with as much rotary motion as

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may be necessary to keep all the substances that may tend to adhere to the sides of the flask in contact with the liquid, throw on a filter of finest linen, and rinse the flask and wash the contents of the filter thoroughly with boiling water. Wash the contents of the filter back into the flask with 200 c. c. of a 1.25 per cent. solution of sodium hydrate, at once raise to boiling, and boil continuously for thirty minutes with rotary motion as above described, filter through a Gooch crucible or according to some similar device, and wash very thoroughly with boiling water. Such thorough washing has been found to be essential to success. Wash then with alcohol and finally with ether, dry at 110°, weigh, incinerate, and give the loss of weight for crude fiber.

*Crude fiber, closed digestion method.**—Pulverize as for the ether extract, and extract the fat at least nearly completely from 2 grams of substance; allow the ether to evaporate, and transfer to a patent-stoppered beer-bottle with the aid of a funnel and 200 c. c. of a solution of 4 per cent. hydrochloric acid in a wash-bottle. Cork, and after seeing that the material is thoroughly saturated with the acid, with none floating on the surface, place in a bath of boiling water of such a size that the neck of the bottle being covered with a copper ring with a suitable-sized hole, the entire bottle, except the upper part of the neck, will be surrounded by the boiling water or steam. At intervals of five minutes the bottle is grasped about the neck with a cloth and given such a rotary motion as to stir up the entire contents and wash down the neck. This is preferable to ordinary shaking. The digestion is continued for one hour and the acid then removed by filtration on finest washed linen, as in the preceding method, and the residue washed back with a wash-bottle into the bottle with 200 c. c. of 4 per cent. solution of *sodic* hydrate, such as the granulated of the Greenbank Alkali Works. The digestion is then continued as before for one hour and the residue collected, as in the preceding method, and thoroughly washed with hot water, alcohol, and ether. It is dried at 110°, weighed, ignited at as low

* Described by Clifford Richardson.

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a heat as possible to prevent volatilization of any soda salts which may not have been removed, and the crude fiber calculated from the loss.

Statement of results.

	In the substance in its natural condition (or as received).	In the dry substance.
Moisture		
Ash		
Ether extract		
Crude fiber		
Crude protein		
Nitrogen: Total		
Albuminoid .		

From Bulletin No. 16, U. S. Dept. of Agriculture.

ABBREVIATIONS OF TITLES OF CHEMICAL JOURNALS.

In the Fifth Annual Report to the American Association for the Advancement of Science the Committee on Indexing Chemical Literature present a provisional list of abbreviations of titles of chemical journals prepared by them in accordance with the suggestion of the chairman at the Buffalo meeting.

In their report the committee give a statement of the principles by which they were governed in drawing up the list, and make the following request: "The committee earnestly desires that their critics, before undertaking further condensation in certain cases which seem to be needlessly extended, shall examine the titles of a compendious bibliography of scientific periodicals. By so doing they will perceive the necessity of differentiation, and that provision has been made to avoid confounding journals having closely similar titles."

The list of abbreviations prepared by the committee is regarded as provisional and is printed in the report in order that it may be submitted to the test of usage. Suggestions will be

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welcomed by the chairman of the committee, who may be addressed care of Smithsonian Institution.

We herewith reprint the list of abbreviations for convenience of our readers; in using it they should note that optional words are placed in parenthesis. For further explanations we refer to the report. The committee is constituted as follows: H. Carrington Bolton, Chairman, F. W. Clarke, Albert R. Leeds, Alexis A. Julien, John W. Langley, Samuel H. Scudder, C. K. Wead.

PROVISIONAL LIST OF ABBREVIATIONS OF TITLES OF CHEMICAL JOURNALS.

The numbers refer to the Catalogue of Chemical Periodicals by H. Carrington Bolton, New York, 1885, 8vo. Titles 183–196 in the Supplement, New York, 1887.

1. Afh. Fys. Kemi.
2. Agenda chim.
3. Chem. Ztg.
4. Allg. chem. Bibl. (Trommsd.)
5. Allg. J. Chem. Scherer
   a. N. allg. J Chem. Gehlen.
   b. J. für Chem. Gehlen.
   c. J, für Chem. Schweigger,
   d. J. prakt. Chem.
6. Alm. di chim. agric.
7. Alm. de chim.
8. Alm. Scheid. Apoth.
   a. Taschenb. f Scheid.
9. Am. Chem. J.
10. Am. Chemist.
11. Am. Lab.
12. Analyst.
13. Ann. Chem. (Liebig). –
14. Ann. chim. phys.
15. Ann. di chim. (Brugnatelli)
16. Ann fis. chim.
17. Ann. Chem. Med.
18. Ann. Chem. Phil.
19. [Refer to 14].
20. Ann. Chym. Pract. Pharm.
21. Ann. Pharm. Bastick.
22. Ann. Phil. (Thomson).
23. Annuaire prod. chim.
24. Annuaire chim.
25. Annuaire sci. chim.
26. Annual Rep. Chem.
27. Anno. alm. pei chim.
28. Anno. chim. ital.
29. Anno. scienze chim. nat.
30. Anno. scienze chim. farm.
31. Anti-Adult. Rev.
32. Arch. der Agr -Chem.
33. Arch. for Pharm. (Trier.)
34. Arch. ges Naturl.
35. Arch. für theor. Chem.
36. Arch. thier. Chem.
37. Arsb. Phys. Chemi.
38. Ausw. Abh. Chem. Crell.
39. Ausw. Ann. Chem. Crell.
40. Beitr. Chem. Wasserberg.
41. Beitr. Min. Klaproth.
42. Beitr. Chem Bucholz.
43. Arch. für physiol. Chem.
44. Ber d. chem. Ges. (*or* Ber.)
45. Berl. Jahrb. Pharm.
46 Bibl. phys. Lit (Hermbstädt.)
   Ann. Chem. Lit.
47. Boston J. Chem.
48. J de pharm.
49. Bull. math. chim (Férussac.)
50. Casopis chem.
51. Centrbl. Agr.-Chem.
52. Chem. Gaz.
   Chem. News.
53. Chem. News Am Repr.
54. Chem. Record. (Lond.)
55. Chem. Rev. (Lond.)
56. Am Chem. Rev.
57. Chem. Kal.
57*a.* Techn.-chem. Jahrb.
58. Chem. Ackersmann.
59 Chem. Ann. Crell.
60. Chem. Ind. (Jacobsen).
61. Chem phys. oefen
62. Chem Archiv. Crell.
63. Chem. J. Crell.
64. Chem.-pharm. archief.
65. Chem. techn. Mitthl.
66. Chem. techn. Repert.
67. Chemist. Mongredieu.

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68. Chemist. Watt.
69. Chem. and Drug.
70. Chem. Advocate.
71. Chem. and Meteor. J. (Amherst.)
72. Chem. Desk Comp.
73. Chemists' J.
74. Chimiste, Bruxelles.
75. Chimiste, Paris.
76. Compt. rend. *or* C. R.
77. C. R. chim. Montpellier.
78. Crell's Chem. J. Lond.
79. Deutscher Chem. Kal.
80. Edinb. J. Sci.
81. Fortschr. techn. Chem.
82. Fortschr. theor. Chem.
83. Fortschr. Chem. Köln.
84. Gazz. chim. ital.
85. Gazz. chim. techn. (Sembenini).
86. Gazz. farm. (Sembenini).
87. Gazz. farm. chim. (Venezia).
88. Giorn. fis-chim. ital.
89. Giorn. chim. veterin.
90. Giorn. farm. chim. (Gajani).
91. Giorn. di farm. Chiappero.
92. Giorn. di farm. Cattaneo.
a. Bibl. di farm.
b. Ann. di farm. appl. (Polli).
93. Giorn. di fis. Majocchi.
94. Giorn. di fis. Brugnatelli.
95. Obs. sur. phys.
a. J. de phys.
96. Jahrb. Erfind.
97. Jahrb. ökon. Chem.
98. Jsb. Agr.-Chem. (Detmer).
99. Jsb. rein. Chem.
100. Jsb. Agr. Chem.
101. Jsb. chem. Techn. (*or* Waguer's Jsb.)
102. Jsb. phys. Wiss. (*or* Berzelius' Jsb.)
103. Jsb. Chem.
104. Jsb. thier Chem.
105, J. chim. phys. Van Mons.
106. J. chim. méd.
107. J. chim. Van Mons.
108. J. der Pharm. Trommsd.
109. J. der Phys. Gren.
a. N. J. der Phys. Gren.
b. Ann. der Phys. Gren.
c. Ann. der Phys. Gilbert.
d. Ann. der Phys. Pogg.
e. Ann. der Phys. Wied.
f. Beibl. Ann. der Phys.
110. J. Phys. Krönig.
111. J. techn. Chem.
112. J. Appl. Chem.
113. Nicholson's J.
114. J. Soc. Chem. Ind.
115. K. phys. chem. Abh.
116. Ztschr. Chem.
117. Laboratorium.
118. Laboratory, Boston.
119. Laboratory, Lond.
120. Listy chem.
121. Mag. f. Apoth. (Elwert.)
a. Repert. f. Chem. (Elwert.)
122. Mag. höhere Naturw.
123. Mech. and Chem.
124. Mél. phys. chim.
125. Mem. prat. chim.
126. Mem. Columb. Chem. Soc.
127. Misc. chim. fis. (Pisa.)
128. Mitthl. Chem. (Kletzinsky).
129. Mitthl. Lab. Chem. Brunn.
130. Monatsh. Chem.
131. Monit. prod. chim.
132. Month. Mag. Pharm.
133. Naturh. chem. Notiz.
134. Mag. für. Pharm. (Geiger.)
135. Orosi.
136. Penny Mech.
137. Pharm. Times.
a. Chem. Times.
138. Pharm. Centrbl.
b. Chem. Centrbl.
139. Pharmacist.
140. Phil. Mag.
141. Piria.
142. Proc. Am. Chem. Soc.
a. J. Am. Chem. Soc.
143. Proc. Chem. Soc.
a. Q. J. Chem. Soc.
b. J. Chem. Soc.
144. Raccolta fis. chim.
a. Ann. fis. Zantedeschi.
145. [Refer to 37.]
146. Recherches phys.-chim.
147. Recueil trav. chim.
148. Rép. chim. Paris.
149. Rép. chim. pure.
Rép. chim. appl.
Bull. Soc. chim. (Paris.)
150. Rép. de pharm. Bruxelles.
151. Rép. de pharm. Paris.
152. Rep. anal. Chem.
153. Rep. chem. Pharm. St. P.
154. Rep. der. Pharm. (Buchner.)
155. Rep. org. Chem. (Lowig.)
156. Rep. Pharm. Russland.
156*A*. Rev. hebd. chim.
157. Rev. Sc. Quesneville.
a. Monit. Sc. Quesneville.
158. Rev. ind. chim.
159. Revista chim.
160. Samml. Abh. Chem. Hochheimer.
161. Scheik. bibl.
162. Scheik. bijdr.
163. Scheik. onderzoek.
164. School Mines Q.
165. Taschenb. scheik.
166. Techn.-chem. Kal.
167. Techn.-chem. Gewerbebl.
168. Techn.-chem. Jahrb.
169. Tekno-kem. J.
170. Tidssk. anv. Chemi.
171. Tidssk. Phys. Chemi.
172. Tijdsch wet. pharm.
173. Toeg. scheik.

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173. *a.* Maandbl. toeg. scheik.
174. N. Gegenst. Chem. (Richter.)
175. Unters. Liebig's Lab.
176. Vjschr. techn. Chem.
177. Yearbook Pharm.
178. Ztschr. anal. Chem.
179. Ztschr. chem. Grossgew.
180. Ztschr. physiol. Chem.
181. Zhurnal Khim.
182. Zpravy Chem.
183. Bull. assoc. chim. France.
184. Bull. Chem. Soc. Washington.
185. Chemiker u. Drogist.
186. Chem.-techn. Centralanz.
187. Deutsche Chem.-Ztg.
188. J. Anal. Chem.
189. Meddel. Carlsberg Lab.
190. N. Y. Analyst.
a. Am. Analyst.
191. Skand. Kem. Centrlblad.
192. Suppl. enciclop. chim.
193. Tokyo K. Kaishi.
194. Vjschr. Chem. Nahr.
195. Ztschr. Chem. Ind.
196. Ztschr. phys. Chem.
Am. J. Sci.
Arch. sc. phys.
Jen. Ztschr.
Sitzb. Akad. Berlin.
Sitzb. Akad. Wien.
Phil. Trans. Lond.
Proc. Roy. Soc.
Proc. Am. Acad.
Ann. N. Y. Acad. Sci.
Proc. Acad. Nat. Sci. Phil.

The number of Society Transactions publishing chemical papers is very great, and the list (added at the suggestion of some members of the committee) could be greatly extended.

THE USE OF AMMONIUM DITHIOCARBAMATE IN ANALYSIS.

By Joseph Klein.

The property possessed by certain sulphides in the moist, freshly precipitated condition of taking up oxygen from the air and becoming soluble, has led to many experiments for devising methods for separating and estimating the heavy metals without the formation of sulphides. Since, in very many cases, either the oxide or the sulphide is the best compound in which to obtain the heavy metals when they are to be weighed, those methods of separation are to be preferred in which the compound obtained is such that it may easily be converted, in the dry way, into oxide or sulphide. To the first category belong, for example, the oxalate methods of Classen; to the latter the Rivot method for separating copper from cadmium and zinc by precipitating the copper with potassium thiocyanate after previous addition of sulphurous acid.

If we consider the salts of the mineral acids which can readily be converted into oxides (nitrates) or into sulphides (sulphates, after addition of sulphur, in a stream of hydrogen) it will be evident that for the formation of oxides only those

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nearly allied to carbonic acid are available ; for sulphides those related to carbon disulphide. The first class comprises the so-called organic acids ; the second class only a few : thiocyanic, thiocarbonic, monothiocarbamic and dithiocarbamic. The property of the thiocyanates, of decomposing at high temperatures only, is one in which they differ from the salts of the three remaining acids derived from carbon disulphide, which form sulphides even in the wet way. Besides, the thiocyanates of most of the heavy metals are soluble in water, a property which excludes them from use in general methods of precipitation and separation. This leaves only the alkaline salts of thiocarbonic, monothiocarbamic and dithiocarbamic acids available as precipitating agents for the heavy metals. The ease with which ammonium dithiocarbamate can be prepared has caused me to test its value for this purpose. Dr. H. Hager has already* pointed out its availability for this purpose ; but I must ascribe this article to an indiscretion, for before Hager employed ammonium dithiocarbamate in place of sulphuretted hydrogen and ammonium sulphide as a means of detecting the heavy metals in official preparations, he had learned from letters that I was busy with an examination of the use of this salt for analytical purposes.

Ammonium dithiocarbamate is formed by the action of carbon disulphide upon an alcoholic solution of ammonia.

$$CS_2+2NH_3=CSNH_2SH,NH_3.$$

Since, however, by the action of these substances upon one another ammonium thiocarbonate is also formed :

$$2CS_2+4NH_3=CS\ (SH.\ NH_3)_2+NH_4SCN$$

the formation of ammonium dithiocarbamate is, therefore, the principal product of the reaction only when certain conditions are maintained.

Upon this subject Debus says† "concentrated solutions, a temperature of 30–40° and excess of ammonia are conditions, which facilitate the formation of ammonium thiocarbonate and ammonium thiocyanate ; dilute solutions of ammonia in alco-

*Pharmaceut. Centralhalle 1885. 430, 458.

† Ann. Chem. 73, 26. See also Jsb. Chem. 849, 1350.

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hol, excess of carbon disulphide and a temperature of 10–15° favor the formation of ammonium thiocarbamate." Although, therefore, both processes take place simultaneously, it is still easy to prepare ammonium thiocarbamate free from ammonium thiocyanate. If we proceed according to Mulder's process,* passing the ammonia from 150 parts of ammonium chloride and 300 parts of caustic lime into 600 parts alcohol and adding 95 parts carbon disulphide, at 30° only ammonium dithiocarbamate will crystallize out; this is collected upon a filter, washed with a little alcohol and dried between filter paper. Any ammonium thiocarbonate which may possibly separate at the same time is recognized by the red color which the crystals take on contact with the air and may be separated mechanically. Only pure ammonium dithiocarbamate was used in the experiments to be described. Presence of ammonium thiocarbonate may easily be detected as follows: When an aqueous solution of nickel sulphate is treated with ammonia until the precipitate formed at first redissolves, the solution diluted with water and a small amount of a solution of potassium (or ammonium) thiocarbonate added, a red zone forms at the point of contact of the two solutions; by shaking, the whole solution is colored red. Ammonium dithiocarbamate does not behave in this way. All my ammonium dithiocarbamate was tested in this way.

Ammonium dithiocarbamate was first obtained by Zeise† who considered it to be hydrosulphide of ammonium thiocyanate (schwefelbrintiges [schwefelwasserstoffiges] schefelblausaures ammoniak). Debus‡ found afterwards that the salt was ammonium thiocarbamate (dithiocarbamate). He also found that the solution of this salt gave with solutions of certain metallic salts compounds which "are characterized generally by their inclination to split up by warming or treatment with alkalies into sulphuretted hydrogen, thiocyanic acid and metallic sulphides." Only the compounds with zinc, copper and lead salts were studied carefully by Debus; he determined the

* J. prakt. Chem. **103**, 178.
† J. fur Chem. Schweigger **41**, 98.
‡ Jsb. Chem. **1849**, 350. Ann. Chem. **73**, 26.

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amount of carbon and hydrogen which they contained by combustion with lead chromate and found that by double decomposition the thiocarbamates of these metals had been formed. For mercuric chloride, nickel sulphate, etc., Debus found only that white and yellowish green precipitates were obtained.

Although for the quantitative estimation of substances, as has been stated in the introduction, it is immaterial in what form the metal may be separated, provided the precipitation and separation is complete and that the compound may readily be converted into oxide or sulphide, I determined first to experiment with copper and zinc salts. A preliminary experiment had shown that the dithiocarbamates of these metals are characterized by great stability; and that a separation might be founded upon the different solubilities of the salts in acids. Moreover, the sulphides of copper and zinc are, in the moist condition, easily decomposed. I may say beforehand, that the precipitation of copper and zinc by ammonium dithiocarbamate surpasses that of the other precipitations in neatness; and that the results will show that the precipitation is complete; and that the conversion into sulphide corresponds to my expectations. In all precipitations a five per cent. solution of ammonium dithiocarbamate was used. This was almost as colorless as water and very stable. Crystallized ammonia dithiocarbamate, on the contrary, decomposes easily; for this reason it is best to keep it in solution and not in the form of crystals. An aqueous solution of ammonium dithiocarbamate which had stood for weeks in a stoppered vessel was entirely unaltered, while the solid salt decomposed in a much shorter time.

ESTIMATION OF COPPER.

If a solution of copper sulphate is treated with a solution of ammonium dithiocarbamate a yellow precipitate of copper dithiocarbamate is obtained.

$$CuSO_4 + 2\ CSNH_2SHNH_3 = Cu\ (CSNH_2S)_2 + (NH_4)_2\ SO_4.$$

If the solution is precipitated while hot and boiled for a few seconds the precipitate separates rapidly and does not stop the pores of the filter. The precipitate is soluble when boiled with a very large amount of hydrochloric acid; treated in

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this way it darkens in color. If ammonia or caustic soda is added to the precipitate while hot it is colored dark at once. The precipitate dissolves easily in nitric acid when heated; red vapors are given off and a yellow body separates—probably sulphur mixed with persulphocyanogen. The precipitate is not changed by standing in the air or by washing; at least I was not able to find a trace of copper in the washings after washing the precipitate for several days. If the precipitate is dried and heated with sulphur in a stream of hydrogen a black residue of cuprous sulphide remains.

For the quantitative estimation 50 c. c. of a copper sulphate solution, which had the strength given below, was diluted with 100 c. c. water and acidified with a little hydrochloric acid. The liquid was then heated to boiling, 30 c. c. of the above mentioned five per cent. solution of ammonium dithiocarbamate solution added and the mixture boiled for 10–20 seconds. After the yellow precipitate had settled it was filtered, well washed with hot water and dried. The dry precipitate, together with the filter ash, was ignited in a porcelain crucible over the blast lamp, with addition of sulphur, in a stream of hydrogen, until the weight became constant. It may be remarked here that the filter may be incinerated most readily and completely in a porcelain crucible.

The estimations in this way gave for 50 c. c. copper sulphate solution the following results: 0.2584, 0.2600, 0.2600 and 0.2600 gms. Cu_2S.

By the estimation of the copper in 50 c. c. with sulphuretted hydrogen 0.2594 gms. Cu_2S, corresponding to 0.8140 gms. $CuSO_4+5\ H_2O$ was obtained.

From the relation

$$\begin{array}{ccc} 499 & : & 159 = 100 : x \\ CuSO_4+5\ H_2O & & Cu_2S \\ & & x = 31.86 \end{array}$$

Using this value of x, from 100 parts of copper sulphate ($CuSO_4+5\ H_2O$) we have obtained according to the above results instead of 31.86 per cent. Cu_2S.

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$CuSO_4+5\ H_2O$ taken.	*Cu_2S Found.*	*Cu_2S corresponding to 100 parts sulphate.*
0.8140	0.2584	31.74
0.8140	0.2600	31.94
0.8140	0.2600	31.94
0.8140	0.2600	31.94

It is evident from these figures that copper may be conveniently separated from its solutions and determined as cuprous sulphide, provided that metals of the sixth, fourth, third, second and first groups are absent. The method may, therefore, be used for the examination of coin silver if only silver and copper are present. The silver is precipitated as chloride from the nitric acid solution in the ordinary way ; the filtrate is then evaporated with hydrochloric acid to drive off the nitric acid and the copper precipitated by ammonium dithiocarbamate. The use of this reagent, however, presupposes the absence of nitric acid and chlorine.

ESTIMATION OF ZINC.

When a solution of zinc sulphate is treated with ammonium dithiocarbamate a white precipitate of zinc dithiocarbamate is formed, which is soluble in an excess of the precipitant. When this clear solution is boiled separation again takes place. Zinc dithiocarbamate is soluble in hydrochloric and nitric acids ; it is insoluble in very dilute acetic acid ; and from weak acetic acid solutions zinc is precipitated by ammonium dithiocarbamate on boiling.

$$ZnSO_4+2CSNH_2SH.NH_3=Zn\ (CSNH_2S)_2+(NH_4)_2SO_4.$$

By standing in the air and by washing with water zinc dithiocarbamate is not affected. At least after standing for hours in the wash water no zinc could be detected in solution. When heated in a stream of hydrogen with sulphur it is converted into zinc sulphide. Since, by continued boiling of zinc dithiocarbamate in an acetic acid solution it is decomposed with formation of zinc sulphide, which runs through the filter because it oxidizes, in the precipitation as dithiocarbamate certain precautions must be observed. These precautions are evident from the following description.

50 c. c. of a solution of zinc sulphate containing 3.5826 gms.

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zinc oxide per liter, corresponding to 12.6715 gms. $ZnSO_4 + 7H_2O$, was treated with sufficient sodium acetate solution to convert the zinc into acetate, and 100 c. c. distilled water and 1 to 1.5 c. c. acetic acid, sp. gr. 1.02, added.* After the fluid was heated to boiling 30 c. c. of the five per cent. solution of ammonium dithiocarbamate was added and the boiling continued for a short time. Immediately after the addition of the ammonium dithiocarbamate the solution became turbid and by boiling the separation of the zinc thiocarbamate was completed; this settled easily and completely when allowed to stand. As soon as no further separation took place—and this point is quickly reached—the solution was allowed to stand and then filtered hot. The precipitate was collected in a filter and thoroughly washed with distilled water, dried, ignited and weighed as directed under copper. Some experience is of course necessary in carrying out this method.

By the use of this method satisfactory results were always obtained. In the filtration the filtrate is generally clear at first; later on it becomes turbid from decomposition of ammonium thiocarbonate and sulphuretted hydrogen. If all the filtrate has passed through the filter and the precipitate is washed with hot water, a clear filtrate is obtained which does not become turbid. If the filtrate runs through turbid from the beginning it is possible that a little zinc sulphide has been formed. This is, however, so small in amount that we may go on with the work without concern and wash the precipitate as above directed. The filtrate and wash water is then evaporated after addition of hydrochloric acid and the solution, after addition of sodium acetate, again precipitated with ammonium dithiocarbamate to throw down the last trace of zinc. In one case, where from the beginning the filtrate ran through turbid, the filtrate and washings were evaporated, with addition of nitric acid to a volume of 15 c. c., the solution filtered and the filtrate precipitated with sodium carbonate. The separated flocculent precipitate of zinc carbonate was filtered through a weighed filter, dried at 100° and found to weigh

* If the solution is carefully neutralized addition of sodium acetate is unnecessary.

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0.0002 gms., corresponding to 0.00013 gms. zinc sulphide. The amount of zinc which passes through the filter is therefore so small that it may almost be neglected in the calculation, as it forms only $\frac{1}{1700}$ part of the entire amount. To determine whether by washing the precipitate of zinc dithiocarbamate goes into solution, the entire quantity of clear wash water was evaporated to a small volume with nitric acid and precipitated hot with sodium carbonate; no separation of zinc carbonate could be detected.

The estimation of zinc by the above method gave for every 50 c. c. zinc sulphate solution the following results:

$ZnSO_4+7H_2O$ *Taken.*	ZnS *Found.*	ZnS *Calculated.*
0.63358	0.2138	0.2141
	0.2138	

From these figures we obtain for 100 parts zinc sulphate ($ZnSO_4+7H_2O$).

ZnS found.	ZnS calculated.
33.74	33.79

SEPARATION OF COPPER FROM ZINC.

The solubility of zinc dithiocarbamate led to the conclusion that ammonium dithiocarbamate might be used for the separation of copper from zinc. The difficulty in the direct separation by means of sulphuretted hydrogen made it necessary to determine carefully whether the separation by means of ammonium dithiocarbamate is a perfect one, and whether small amounts of zinc would not be carried down with the copper. This was investigated as follows:

50 c. c. zinc solution and 50 c. c. copper sulphate solution were mixed and diluted with 200 c. c. distilled water. After the addition of 10 c. c. hydrochloric acid, sp. gr. 1.05 the solution was heated to boiling, to the hot solution 40 c. c. of the five per cent. ammonium dithiocarbamate solution added with constant stirring, the solution again boiled for a few seconds and, after standing for short time, filtered. The precipitate was brought on the filter and washed carefully with hot water containing a little hydrochloric acid until the filtrate

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no longer contained sulphuric acid. The copper dithiocarbamate was dissolved in nitric acid, the filtered solution evaporated to dryness with HCl, taken up with HCl, diluted, and the copper precipitated with potassium thiocyanate after addition of sulphurous acid. The filtrate from the cuprous thiocyanate was then precipitated while hot with sodium carbonate, the precipitate washed by decantation, brought into a porcelain crucible, dried and ignited in a stream of hydrogen. After cooling the contents of the crucible were dissolved in a little dilute sulphuric acid and the solution precipitated while hot with sodium carbonate. A small separation of zinc carbonate took place, the amount of which, however, fell short of a milligramme. (This estimate was made by comparison with the previously mentioned amount of 0.0002 gms. zinc carbonate.)

By a single precipitation, then, the separation of zinc from copper is incomplete. In a second experiment with 50 c. c. zinc and copper solutions, the precipitated copper dithiocarbamate was redissolved in nitric acid and the solution evaporated twice with HCl and then precipitated with ammonium dithiocarbamate. The separated copper salt was now found to be entirely free from zinc; this was determined in the same manner as before.

When the copper has been freed from zinc by two precipitations, all the zinc will be contained in the first and second filtrates. These are evaporated and more ammonium dithiocarbamate added to ascertain whether all the copper has been thrown down. The zinc may then be separated by either of two methods: as basic carbonate or as dithiocarbamate. In the first case we must consider the action of sodium carbonate upon a solution of zinc containing ammonium thiocyanate, for in the precipitation of copper, by the action of hydrochloric acid upon the excess of ammonium dithiocarbamate ammonium thiocyanate is formed.

$$CS.NH_2SH.NH_3 = H_2S + CNSH.NH_3.$$

If we add ammonium thiocyanate to a zinc solution and then sodium carbonate there is formed, according to the

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amount of ammonium thiocyanate added, either an incomplete precipitate, or no precipitate at all. Ammonium thiocyanate, therefore, behaves like other ammonium salts.

In precipitating with sodium carbonate we must proceed, then, in the same manner as when other ammonium salts are present.* To destroy the thiocyanic acid we can evaporate with nitric acid.

If the zinc is to be precipitated by ammonium dithiocarbamate the united filtrate is evaporated, the HCl neutralized and the rest of the process conducted as described under estimation of zinc.

With 50 c. c. each of copper and zinc solutions the following results were obtained :

Quantity used of sulphate of	*Sulphide found.*	*Sulphide calculated.*
Cu: 0.8140	0.2574	0.2594
Zn: 0.63358	0.2130	0.2141

Calculated for 100 parts of the salt mixture these figures give :

	Found.	*Calculated.*
Cu_2S	17.71	17.98
ZnS	14.71	14.79

ANALYSIS OF BRASS.

If the brass contains only copper and zinc the estimation of both elements is conducted as above described. The alloy is dissolved in nitric acid and this solution evaporated with HCl to drive off the nitric acid. The hydrochloric acid solution is now diluted with water so that about 0.3 gms. brass is contained in 300 c. c. The total amount of hydrochloric acid present should be about 10–15 c. c., sp. gr. 1.05, for this amount of brass. The copper is now twice precipitated hot with ammonium dithiocarbamate, dried and ignited with sulphur in a stream of hydrogen. The united filtrates from the copper are evaporated, neutralized with sodium carbonate, acidified with acetic acid and again treated with ammonium dithiocarbamate to separate the zinc. The zinc salt is dried

* Attention has been given to the presence of ammonium salts in former tests. Compare "estimation of zinc" and "separation of copper from zinc."

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and converted into sulphide, or the zinc is precipitated from the united filtrates with sodium carbonate in the usual way and weighed as zinc oxide. The analysis of brass by this method gave the following results:

Brass taken.	*Found*		*Per Cent.*	
	Cu	*Zn*	*Cu*	*Zn*
0.3470	0.208405	0.139379	60.05	40.16
0.30912	0.18585	0.123630	60.12	39.99

ESTIMATION OF NICKEL AND COPPER (NICKEL COINS).

These coins are treated in the same way as brass before precipitating the copper. The copper is precipitated from hydrochloric acid solution by means of ammonium dithiocarbamate and the precipitation repeated. From the filtrate the nickel is precipitated with caustic soda.

Coin used.	*Content in*		*Per cent.*	
	Cu	*Ni*	*Cu*	*Ni*
0.2912	0.218147	0.072766	74.91	24.98

SEPARATION OF COPPER FROM IRON, MANGANESE, NICKEL AND COBALT.

As iron, manganese, nickel and cobalt are not precipitated from hydrochloric acid solution by means of sulphuretted hydrogen, neither are they precipitated by ammonium dithiocarbamate, provided that the solutions are treated with the reagent while hot and that sufficient hydrochloric acid is pressent. This behavior made it seem probable that ammonium dithiocarbamate could be used for separating copper from iron, manganese, nickel and cobalt. Cobalt, however, shows this peculiarity; that with hot solutions and when the boiling has not been continued too long the color is changed to green. Only by continued boiling does the color again become red.

The separation of copper from iron, manganese, nickel and cobalt was tested as follows: From the hot solution copper was precipitated by ammonium dithiocarbamate. The precipitate was dissolved in nitric acid and precipitated a second time with sulphuretted hydrogen. The filtrate from the copper sulphide was found to be free from iron, manganese, nickel and cobalt. On account of the peculiar behavior of the cobalt,

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above noted, special tests are necessary, to determine whether its separation from copper is complete in all cases.

SEPARATION OF COPPER FROM BARIUM, STRONTIUM, CALCIUM AND MAGNESIUM.

The dithiocarbamates of the alkaline earths are, like those of the alkalies, soluble in water. The possibility of a complete separation of copper from barium, strontium, calcium and magnesium was therefore indicated. The tests, which were carried out by dissolving the copper dithiocarbamate in nitric acid and reprecipitating the copper with sulphuretted hydrogen, the filtrate being examined for the alkaline earths, showed that in dilute solutions and when not too large an amount of alkaline earth is present the separation is complete. If, however, much of the alkaline earth is present it is best to precipitate the copper a second time. All the alkaline earth will then be found in the filtrates from the first and second precipitate.

SEPARATION OF COPPER FROM THE ALKALIES.

What has been said of the separation of copper from the alkaline earths applies also to the separation of copper from the alkalies.

SEPARATION OF ZINC FROM THE ALKALINE EARTHS.

The zinc dithiocarbamate separated from a weak acetic acid solution was dissolved in nitric acid and precipitated with ammonium sulphide after addition of ammonia and ammonium chloride. The filtrate from the zinc was then evaporated and tested for barium, strontium and calcium. The results corresponded with those obtained with copper and alkaline earths; in concentrated solutions and in presence of much alkaline earth the zinc is not pure, while in dilute solutions the separation is a perfect one.

SEPARATION OF ZINC FROM THE ALKALIES.

The statements made for the separation from the alkaline earths also apply here.

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ACTION OF AMMONIUM DITHIOCARBAMATE UPON THE ELEMENTS OF THE THIRD GROUP: ALUMINUM AND CHROMIUM.

The action of ammonium dithiocarbamate upon chromium and aluminum is of great interest, as these metals are precipitated from their solutions by the reagent. If ammonium dithiocarbamate is added to not too concentrated a solution (see below) of aluminum sulphate or chromium chloride in the cold no change takes place; but on heating the solution becomes turbid, and sulphuretted hydrogen is given off. If the boiling is continued aluminum separates as a white precipitate, which is probably pure aluminum hydroxide. Chromium does not behave quite the same; by heating the mixture with chromium salt the liquid first loses color, then takes a very beautiful blue color while chromium hydroxide separates. In the precipitate blue crystalline particles can be detected, mixed with the chromium hydroxide. These are the cause of the blue color of the solution. The filtrate is also colored blue and is decomposed by addition of ammonia and further heating, more chromium hydroxide separating. The blue particles differ from chromium hydroxide in being almost insoluble in cold HCl. They are readily dissolved by water, especially when the water is warmed. The slight solubility in HCl may be used to separate the blue particles from the chromium hydroxide. Under certain conditions the blue precipitate separates in an amorphous form. By prolonged boiling with ammonia or caustic soda the blue substance is decomposed with separation of chromium hydroxide. If the solution is then filtered and a little sodium nitroprusside added to the filtrate the characteristic sulphur reaction is obtained; if another portion of the filtrate is acidified and a little ferric chloride added thiocyanic acid can be detected. It is possible, therefore, that the blue substance is chromium dithiocarbamate; a quantitative estimation of the constituents will be necessary to determine this.

This statement apparently contradicts that of Debus,* that by mixing chromium sulphate with ammonium dithiocarba-

* loc. cit.

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mate colorless crystalline needles containing chromium and sulphur are obtained. Such crystals are formed when somewhat concentrated solutions of the above substances are mixed; if allowed to stand in the cold for several hours the above described blue coloration takes place, and the white crystals of Debus become mixed with blue crystals containing sulphur and the elements of thiocyanic acid. Debus does not appear to have observed the formation of the blue crystals.

The white crystals of Debus are also different from the blue crystals, in that they dissolve completely in warm caustic soda to a yellow liquid, while by similar treatment the yellow crystals give chromium hydroxide. In all their chemical and physical relations the crystals of Debus resemble free dithiocarbamic acid as it separates out in crystalline form when hydrochloric acid is added to solutions of ammonium dithiocarbamate. The observation that the crystals contain chromium can only have been caused by the presence of chromium as an impurity. I have often observed these crystals in adding solutions of metallic salts to ammonium dithiocarbamate in the cold and allowing the clear solution, or the clear filtrate, to stand; acid reaction appears, however, to be necessary.

I may observe that the solubility of dithiocarbamic acid in water is not so great as given by Mulder*; the crystals may, rather, be warmed slightly with much water without dissolving completely; if the solution is heated too strongly complete decomposition takes place.

The observed behavior of aluminum and chromium salts with ammonium dithiocarbamate can only be explained by supposing that first the dithiocarbamates of aluminum and chromium are formed, and that these then decompose with evolution of sulphuretted hydrogen, formation of thiocyanic acid and separation of the hydroxides of the two metals.

$$Al(S.CS.NH_2)_3 + 3H_2O = Al(OH)_3 + 3H_2S + 3HCNS.$$

The formation of the blue chromium crystals, more than the separation of sulphuretted hydrogen, favors this view.

If an acid or alkaline solution of chromic acid is treated with

* loc. cit.

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ammonium dithiocarbamate and warmed, reduction of the chromic acid takes place and a chromic salt remains in solution if the solution was acid, or chromium hydroxide separates if the solution was alkaline. Reduction also takes place slowly in the cold. Ammonium dithiocarbamate, therefore, behaves likes sulphuretted hydrogen to chromic acid.

ACTION OF AMMONIUM DITHIOCARBAMATE ON THE ELEMENTS OF THE FOURTH GROUP: IRON, NICKEL, COBALT, MANGANESE, ZINC AND URANIUM.

The behaviour of ammonium dithiocarbamate with the metals of the fourth group has already been noted in part in the account of the separation of copper from these elements; in hydrochloric acid solution these elements are not precipitated on heating, corresponding to their behaviour with sulphuretted hydrogen. If the solution is cold, precipitation sometimes takes place (Nickel) and sometimes it remains clear (Manganese). Ammonium dithiocarbamate does not, however, give very well characterized reactions with the members of this group. The reactions are almost always those which might be expected. Neither is there anything characteristic in the behavior of ammonium dithiocarbamate towards the double cyanides.

Iron. Ferric salts are reduced by ammonium dithiocarbamate with separation of sulphur, just as they are reduced with sulphuretted hydrogen. If the reagent is added to ferric chloride in excess a dark precipitate forms; if the proceeding is reversed and a little ammonium dithiocarbamate added to an excess of ferric chloride the mixture remains clear at first; soon, however, it becomes turbid, through separation of sulphur, and the filtrate gives a blue precipitate with potassium ferricyanide. No precipitate is formed by warming an acetic or hydrochloric acid solution with ammonium dithiocarbamate. The dark precipitate formed by the ammonium salt in ferric solutions is completely soluble in warm HCl. Ferrous salts give, if they are acidified, and if too much reagent is not present, no precipitate; upon addition of ammonia a dark precipitate is formed.

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Nickel. In neutral and acid solutions nickel sulphate gives a yellowish-brown precipitate with ammonium dithiocarbamate. If the precipitate is filtered off and washed with water it has a uniform light green color. This was observed by Debus and described in his article already referred to. By heating with hydrochloric acid the precipitate redissolves; by heating with acetic acid only a part dissolves, the remainder becoming darker. On the contrary, from a solution containing sodium acetate and acetic acid, nickel is incompletely precipitated by ammonium dithiocarbamate in a hot solution. This is caused by the ammonium thiocyanate formed which prevents the precipitation of nickel sulphide; upon this fact Zimmerman has founded a method* for the separation of zinc from nickel, cobalt, etc., with sulphuretted hydrogen in presence of ammonium thiocyanate. A dark solution and precipitate are also obtained when ammonium dithiocarbamate is added to an ammoniacal nickel solution, corresponding to the precipitation of nickel with ammonium sulphide. If potassium cyanide is added in excess to a nickel solution, so that a clear solution is obtained, the reagent gives no precipitate. The behavior of an ammoniacal nickel solution towards ammonium dithiocarbamate, and the difference in behavior between this and ammonium thiocarbonate, has already been mentioned in describing the test for the purity of ammonium dithiocarbamate.

Cobalt. What has been said of the behavior of nickel sulphate with the reagent, applies nearly always to cobalt chloride. The precipitations from acid and ammoniacal solutions are not complete, the filtrate from the precipitate is always colored. Neither is the precipitation from acetic acid solutions complete, because ammonium thiocyanate interferes with, or entirely prevents, the precipitation of cobalt by sulphuretted hydrogen. From the double cyanide cobalt, like nickel, is not precipitated by ammonium dithiocarbamate.

Manganese. Neutral and acid solutions are not precipitated by the reagent. If, however, ammonium chloride is added

* Ann. Chem. **199**, 1.

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to a solution of manganese sulphate, in such quantity that no precipitate forms on the addition of ammonia, and then ammonium dithiocarbamate, at first no precipitate forms; if the solution is heated a white precipitate is formed which becomes flesh colored by continued heating. This precipitate is soluble in hydrochloric, nitric and acetic acids.

Zinc. The behavior of zinc towards ammonium dithiocarbamate was given, in part, in describing the estimation of zinc; only a few things remain to be added to what was there said: A solution to which potassium cyanide has been added gives no precipitate with the reagent. Zeise says* that crystals are formed when zinc solutions are treated with ammonium dithiocarbamate; Debus† has not observed these crystals. I have repeatedly obtained, under certain conditions, zinc dithiocarbamate in crystals, which oftentimes had a length of several millimeters. These crystals were formed, especially, when a solution acidified with acetic acid and containing so much ammonium dithiocarbamate that the precipitate formed was only partly redissolved, was heated. The precipitate may then either dissolve completely, or a part remain undissolved—in either case the zinc separates out on boiling in pointed crystals of zinc dithiocarbamate.

Uranium. Debus states that uranium nitrate is colored blood red by ammonium dithiocarbamate, without formation of a precipitate. This is true only if the mixture is cold; if it is heated to boiling it becomes turbid and uranium separates as a grayish-black precipitate. The filtrate is nearly colorless with a slight tinge of yellow. The grayish-black precipitate is also formed in an acetic acid solution; but if free hydrochloric acid is present only sulphur separates. The red color of the uranium solution which has been treated with ammonium dithiocarbamate disappears when ammonium carbonate is added and a clear yellow solution results. If, therefore, a uranium solution is treated with ammonium carbonate in excess it does not become blood-red on addition of ammonium

* Debus, Ann. Chem. 73, 26.
† Ann. Chem. 73, 26.

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dithiocarbamate. This solution may be heated, if some care is taken, without becoming turbid.

A consideration of the results of the action of ammonium dithiocarbamate upon the solutions of metals of the fourth group makes it appear possible that the precipitation of zinc from an acetic acid solution, and the non-precipitation of manganese from acetic acid solutions may lead to a separation of manganese from zinc. Experiments tried for this purpose showed that even with small quantities of manganese the zinc precipitate contained manganese. By treating the zinc precipitate with nitric acid and red lead manganese could always be detected.

ACTION OF AMMONIUM DITHIOCARBAMATE UPON THE ELEMENTS OF THE FIFTH GROUP: MERCURY, LEAD, SILVER, BISMUTH, COPPER AND CADMIUM.

Some of the reactions with elements of the fifth group have already been carried out by Debus and the precipitates obtained described. These reactions are those of ammonium dithiocarbamate with mercury, copper, and lead salts. The precipitates obtained are white to yellow. Some of these become darker on standing, some of them are permanent, as in case of copper. The decomposition takes place more rapidly by boiling than by simply allowing to stand and is almost instantaneous upon addition of caustic soda in the cold. With mercury, copper and cadmium, the behavior when treated with potassium cyanide in excess and ammonium dithiocarbamate must be considered.

Mercury. The white cheesy percipitate obtained in neutral or hydrochloric acid solution with ammonium dithiocarbamate, which, as above mentioned, decomposes easily, is soluble in nitric acid. If the precipitate is boiled with moderately concentrated hydrochloric acid a small part goes into solution. If mercuric chloride is treated with potassium cyanide in excess no precipitate forms on addition of ammonium dithiocarbamate. Mercuric cyanide is, however, precipitated by ammonium dithiocarbamate. With mercurous nitrate a black precipitate of metallic luster is obtained. Debus con-

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siders that the precipitate with mercuric chloride contains mercurous chloride.

Lead. The yellowish white precipitate obtained by treating lead acetate with the ammonium salt becomes red by drying (Debus), and decomposes by boiling, as well as by treatment with ammonia or caustic soda. By treatment with ammonia the precipitate becomes first red, then passes through brown to black. The white precipitate is soluble in warm nitric acid; it dissolves also in tolerably concentrated hydrochloric acid.

Silver. The yellowish-white precipitate changes almost immediately after precipitation to a dark color, if silver nitrate is in excess. If, however, a little silver nitrate is added to a solution of ammonium dithiocarbamate, or ammonium dithiocarbamate is added in excess immediately, the yellowish-white precipitate is tolerably permanent. It is, however, quickly changed by ammonia or caustic soda. It is soluble in nitric acid. In a solution of silver to which potassium cyanide has been added in excess ammonium dithiocarbamate gives no precipitate.

Bismuth. Bismuth chloride solution is colored yellow by ammonium dithiocarbamate. If the precipitate is boiled with dilute hydrochloric acid it is partly redissolved. In its behavior to ammonia and caustic soda, what has been said of the other metals applies here.

Copper. In this precipitate also, as already stated (see estimation of copper), decomposition takes place on addition of ammonia and caustic soda. A solution to which potassium cyanide has been added in excess is not precipitated by ammonium dithiocarbamate. By boiling with concentrated hydrochloric acid small quantities of copper dithiocarbamate are dissolved.

Cadmium. The precipitate obtained with ammonium dithiocarbamate is white and appreciably soluble in boiling hydrochloric acid. The precipitate is decomposed, slowly when boiled alone, rapidly by boiling with ammonia or caustic

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soda. No precipitate is formed in a solution to which potassium cyanide has been added.

If the precipitates obtained as above are compared with those produced by sulphuretted hydrogen considerable similarity is noticed. The small solubility of the copper precipitate in hydrochloric acid and the great solubility of the lead precipitate are in both cases analogous. The behavior of the double cyanide towards ammonium dithiocarbamate is, however, different from that with sulphuretted hydrogen. The double cyanides of mercury copper and cadmium especially, are not precipitated by ammonium dithiocarbamate. The method used in the quantitative separation of copper and cadmium, by dissolving in potassium cyanide and adding sulphuretted hydrogen or ammonium sulphide has its analogue with ammonium dithiocarbamate, if, after the addition of the ammonium dithiocarbamate a sufficient amount of ammonia is added and the solution warmed. The cadmium then separates as a yellow precipitate while the copper remains in solution. In the separation of copper from mercury caustic soda is to be preferred for the decomposition of the double mercuric cyanide by ammonium dithiocarbamate is very slow. From the filtrate from cadmium sulphide or mercury sulphide the copper may be thrown down by addition of hydrochloric acid as copper dithiocarbamate.

ACTION OF AMMONIUM DITHIOCARBAMATE UPON SOLUTIONS OF THE OXIDES OF THE SIXTH GROUP: ARSENIC, ANTIMONY AND TIN.

The reactions with arsenious acid, antimony chloride and stannic chloride have already been ascertained by Debus and briefly described.

Arsenic. According to Debus arsenious acid gives with ammonium dithiocarbamate a white precipitate. This happens, however, only under certain conditions. If arsenious acid is mixed with ammonium dithiocarbamate in aqueous solution no precipitate is formed at first; after some time, however, the liquid becomes turbid and a yellow precipitate separates—probably arsenic sulphide. By boiling the clear solu-

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tion this separation takes place at once. The yellow precipitate is soluble in ammonia and ammonium carbonate. Acid solutions behave quite differently. Upon addition of hydrochloric, sulphuric or acetic acid to the mixture of aqueous solutions of the two substances a white cheesy precipitate is produced. If this is filtered the filtrate gives no precipitate with sulphuretted hydrogen. The well-washed precipitate decomposes when boiled with water, with evolution of carbon dioxide and sulphuretted hydrogen and probable formation of arsenic sulphide. Free thiocyanic acid could not be detected. The white precipitate is soluble in ammonia, ammonium carbonate and caustic soda. By boiling with caustic soda no ammonia is liberated. In the cold hydrochloric acid again separates the white compound, apparently unchanged. If, after the white precipitate has been boiled with water, caustic soda is added and the solution again boiled ammonia is given off. If the solution is then acidified and boiled vapors of thiocyanic acid are given off. From these reactions it is evident that the compound contains neither ammonia nor thiocyanic acid, but that these are formed by heating it with water. These reactions as well as the evolution of carbon dioxide and sulphuretted hydrogen are shown by free dithiocarbamic acid. No mention of this peculiar decomposition is to be found in the literature.

Arsenic acid is precipitated by ammonium dithiocarbamate in acid solution. The precipitate is white with a tinge of gray. It is soluble in ammonia, ammonium carbonate and caustic soda, and decomposed by boiling with water in the same way as the precipitate from arsenious acid.

Antimony. A yellowish-white precipitate is thrown down from an antimony chloride solution by ammonium dithiocarbamate which is soluble on heating in ammonia and caustic soda. From the cold solutions upon addition of hydrochloric acid the yellowish-white precipitate again separates, apparently unchanged. By heating with water the same reactions take place as with arsenious and arsenic acids. Antimony pentachloride behaves in the same way to ammonium dithiocarba-

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mate. The precipitate is yellowish-white, cheesy, soluble in caustic soda and ammonia and is decomposed by boiling. The decomposition products here also, are carbon dioxide, sulphuretted hydrogen, a little (traces) thiocyanic acid, antimony sulphide and ammonium thiocyanate.

Tin. A solution of stannous chloride acidified with hydrochloric acid gives with ammonium dithiocarbamate a yellow, somewhat orange-colored precipitate, which is soluble in caustic soda and separates, apparently unchanged, on addition of hydrochloric acid. The precipitate is also soluble in ammonia, but the solution soon turns dark and becomes turbid—probably from the separation of brown stannous sulphide. If the yellow precipitate is boiled with water, carbon dioxide and sulphuretted hydrogen are given off and in the filtrate ammonia can be detected; after acidification thiocyanic acid can be detected with ferric chloride.

Stannic chloride is precipitated yellow by ammonium dithiocarbamate. The precipitate is, when freshly precipitated, soluble in ammonia and caustic soda. By boiling with water it decomposes with evolution of sulphuretted hydrogen and carbon dioxide.

The above reactions show that the action of ammonium dithiocarbamate upon the different compounds of arsenic antimony and tin is perfectly similar. With each white, or more or less yellow compounds are formed, which, when freshly precipitated, are soluble in ammonia and caustic soda. The dried precipitates behave differently, since by drying and indeed even by washing decomposition of the precipitates take place. When the arsenious and arsenic acid precipitates are dissolved in ammonia more or less sulphur always remains. Arsenic acid is reduced to arsenious acid. The want of uniformity in these compounds is shown by the following determinations:

I.—Sb_2O_5 compound. Antimony found:
29.98 per cent. 29.97 per cent.

II.—Sb_2O_3 compound. Antimony found:
68.19 per cent. 75.81 per cent.

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III.—SnO_2 compound. Tin found:

25.18 per cent. 25.22 per cent.

While the first and third compounds give results which agree well, the second shows too large a variation in the amount of antimony. These compounds after precipitation and washing were dried, first on tiles and then in the desiccator over sulphuric acid. The estimation was conducted by oxidizing the substance in a porcelain crucible, first with dilute, then with stronger, and, finally, with concentrated nitric acid, the rest of the operation being performed in the usual way. The figures obtained for the antimony compound correspond well with those required by the formula $Sb_2O_4 5CS_2NH_3$, a compound in which the conditions are present of the easy formation of Sb_2S_3. Whether this is actually the formula cannot be decided. The figures obtained for the antimony trioxide compound, as well as those for the stannic oxide compound, do not give a constitution analogous to the one above. In the dry substances it is easy to detect with the naked eye two substances, differently colored.

By boiling the dithiocarbamate precipitate of the sixth group with water the same decomposition products are formed: sulphuretted hydrogen and carbon dioxide. Thiocyanic acid could often be detected in the vapors given off, but ammonia never; neither was ammonia obtained by boiling with caustic soda; if, however, the precipitate was boiled with water and then with caustic soda, ammonia was given off. If, in plaee of caustic soda, or, after boiling with caustic soda, sulphuric acid was added, thiocyanic acid could be easily detected in the vapors given off. As already observed, when speaking of the compound with arsenious acid, free dithiocarbamic acid behaves in the same way.

That arsenic can be precipitated by ammonium dithiocarbamate appears to me to be worthy of note for another reason. Numerous methods have been given for the preparation of arsenic-free sulphuretted hydrogen. If careful examination should show that ammonium dithiocarbamate could be used with advantage in toxicological analysis, further work in the

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preparation of arsenic-free sulphuretted hydrogen would be superfluous. Carbon disulphide and ammonia free from arsenic are easily obtained.

REP. ANAL. CHEM.

DETERMINATION OF PHOSPHORUS BY THE CITRIC ACID METHOD.

BY LEE S. CLYMER.

WHILE many methods have been given for the determination of phosphorus by the molybdate and magnesia methods, comparatively little has been said about the citric acid process.

This method, with slight modifications, is used in a great many of the technical laboratories, and when skillfully manipulated gives accurate results.

Its advantage over the molybdate and magnesia method is its shortness and cheapness. A determination started in the morning can easily be completed the next morning, and when many determinations are made by the molybdate and magnesia method, the molybdic acid used becomes quite an item in the running expense of the laboratory.

PROCESS.

Dissolve 5 gms. iron or steel in 40 c. c. of nitric acid, sp. gr. 1.20, in a tall beaker covered with a watch glass. When in solution transfer into a three-and-a-half inch porcelain evaporating dish and evaporate to dryness over a Bunsen burner. A little care must be exercised to avoid spattering towards the end of the evaporation. Heat until the smell of acid has disappeared. Let the dish cool ; add 30 c. c. of strong hydrochloric acid and evaporate down until ferric salt begins to separate. Dilute slightly with water and filter off the graphite. This may be quickly done by using the cotton filter described by A. B. Clemence, this Journal, vol. 1, part 3, p. 273. Add ammonia until alkaline. Now add an excess of ammonium bisulphite, about 5 c. c. of the concentrated solution will ordinarily be sufficient. Add ammonia and hydrochloric acid

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alternately until all the iron is reduced to the state of proto-salt.

The alternate addition of NH_4OH and HCl is to promote the reduction of the ferric salt which takes place rapidly at or near the neutral point. When the ferric salt is finally all reduced the solution will have a greenish tint.

The excess of SO_2 must now be driven off. This may be done by adding a small crystal of potassium chlorate to the solution ; after the addition, NH_4OH and HCl must be alternately added to see if the small amount of ferric salt formed is reduced ; if so, the presence of SO_2 is indicated and another small crystal of potassium chlorate must be added and the same operation repeated until the faint yellow of the solution is no longer bleached upon the alternate addition of NH_4OH and HCl. The presence of SO_2 may also be detected by its odor in an acid solution. When the solution is free from sulphur dioxide and only a small portion of the iron is in the ferric state, neutralize with ammonia, add sodium acetate and boil for a few minutes. The whole of the phosphorus, as phosphate of iron, and the small amount of ferric iron is precipitated as basic acetate, the ferrous iron remaining in solution. Let the precipitate settle, filter, and wash with water. The filtrate as it runs through must be clear, though after standing it becomes turbid, due to oxidation. Dissolve the precipitate on the filter with about 10–15 c. c. of strong HCl and dissolve about 5–7 gms. of citric acid in the filtrate ; make strongly alkaline with ammonia and add a few cubic centimeters of magnesium mixture. Cool, and *stir* until a precipitate of magnesium ammonium phosphate appears. This often requires ten to fifteen minutes constant stirring. Let stand all night, filter, ignite in perfectly clean platinum crucible and weigh. Dissolve the precipitate of magnesium pyrophosphate with strong HNO_3 in crucible, filter, ignite residue in same crucible, weigh and subtract the second weight from the first, and the difference will be the weight of $Mg_2P_2O_7$.

LABORATORY OF COOPER & HEWITT, RIEGELSVILLE, PA.

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COLORIMETRIC CARBON ESTIMATION.

By Fred. F. Sharpless.

In laboratories connected with Bessemer converters, where a great number of carbon estimations are daily made, it is preferable to use a set of standard colors, which may be used from day to day, than to dissolve standard steel for comparison. This has long been practiced in many of our best laboratories but with varying success. Organic colors, as those made from coffee, caramel, etc., change so rapidly while fresh that no dependence can be placed upon them, but when old are quite reliable and may be used with advantage for steels high in carbon.

Colors composed of inorganic salts have not, if properly made, the disadvantage of changing rapidly; they may be made up in a short time, and by their use the delicate shades of brown, amber, and green may be obtained much better than by the use of the mentioned organic colors.

At the Duluth meeting of the Am. Institute of Mining Engineers, July, 1887, Mr. Theo. Robinson, of Joliet, read a paper on standard carbon colors made from copper, cobalt and ferric chlorides. He makes a strong solution of each of these salts in slightly acidified water, and from these three, with water, makes two solutions, one corresponding to a "brown .50 carbon" and the other corresponding to a "green .30 carbon," and again mixes definite quantities of these two solutions together with water to form all intermediate colors. I found his method worked well, but have far less trouble and obtain much more satisfactory results with the following method:

Cobalt chloride—25 gms. of the salt dissolved in 50 c. c. water and .5 c. c. 1.20 HCl.

Copper Chloride—50 gms. of the salt dissolved in 100 c. c. water and 1 c. c. 1.20 HCl.

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Ferric Chloride—50 gms. of the salt dissolved in 100 c. c. water and 1 c. c. 1.20 HCl.

In steels low in carbon there is a predominance of the green color of ferrous nitrate which is gradually obscured as the carbon increases. This color is, however, still present, and it is partially due to it that we get the dull amber so hard to imitate. The green, if we always take the same weight of steel, must be constant and the variation of color is then due to the amount of combined carbon present.

Working upon this assumption, I separated the color due to the carbon from the HNO_3 solution of the steel by means of sodium hydrate according to Steads' method. The soda takes up the coloring matter intensifying it, but not changing its shade.

I now added to acidified water (1 c. c. of 1.20 HCl to 50 c. c. water), drop at a time, small quantities of the three salts until a solution was obtained which exactly corresponded in shade to the acidified soda solution.

The relative proportion of these salts finally adopted was 5 c. c. $CuCl_2$, 19.2 c. c. Fe_2Cl_6, and 16.4 c. c. $CoCl_2$; a solution made up in this way gave me a greenish brown color which I called my "day-carbon-color."

I now dissolved pure iron wire, or one which would give no carbon colorimetrically, and obtained by itself the color of the nitrates of iron produced in this process, and also made a standard corresponding in shade and intensity to this.

The proportion of salts and water in this case was 280 c. c. acidulated water, 3.4 c. c. $CuCl_2$, 15.8 c. c. Fe_2Cl_6 and 5 c. c. $CoCl_2$; this I called the "day-iron-color."

I used for standards a .35 and a .49 carbon steel, dissolved .5 gm. in 12 c. c. 1.20 HNO_3 in the cold until action ceased, then heated to a temperature of 98° or 100° for 15 minutes, plunged into a cold bath for a minute and then filtered through dry filters into dry test tubes.

The color corresponding to that of the steel was made by running into 7 c. c. of the "day-iron-color" the "day-carbon-color" until they exactly matched in intensity.

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If the "day-carbon-color" is correctly made they will match both in shade and intensity, but, as the salts used are very deliquescent, the composition varies and will hence vary the strength of their solutions, and the shade of those made up from them; so it may be found necessary to add a drop or two of iron, cobalt or nickel to the standard being produced, after which a corresponding addition is made to the whole of the "day-carbon-color." It will now be found that by adding a few drops of this solution to a given number of cubic centimeters of the "day-carbon-color" any desired standard may be produced.

To produce a color matching the .35 carbon in daylight, I used 7 c. c. of the "day-iron-color" and 1.8 c. c. "day-carbon-color."

For a .49 carbon color I used 7 c. c. of the "day-iron-color" and 3.7 c. c. "day-carbon-color."

The amount of "carbon color" used for each point is not constant but increases a trifle with every additional hundredth of carbon.

From these data I prepared intermediate standards and on dissolving intermediate steels found them to compare to a nicety.

Where much of this work is done, as around converters, it is necessary to work at night; here all lights, excepting magnesium (according to Mr. Robinson), cause the solution to appear of a different color from that observed in daylight. For night work I prepared a "night-iron-color" and a "night-carbon-color" in the same way as I did the day colors, but worked behind gas light.

The "night-iron-color" was made from 70 c. c. water (acidulated), 2.7 c. c. Fe_2Cl_6, .9 c. c. $CuCl_2$, and 1.7 c. c. $CoCl_2$.

The "night-carbon-color" was made from 32 c. c. $CoCl_2$, 4 c. c. $CuCl_2$ and 10.5 c. c. Fe_2Cl_6.

To obtain a color corresponding to a .43 carbon steel I used 7 c. c. of the "night-iron-color" and 1.1 c. c. "night-carbon-color."

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To obtain a color corresponding to a .49 carbon I used 7 c. c. "night-iron-color" and 1.65 c. c. "night-carbon-color." Colors made from these data corresponded exactly with intermediate steels.

This scheme is theoretically better than many in use and offers also practical advantages.

After the "carbon" and "iron colors" are once made only two solutions are used for making up the standards, and the amount of one of these is always constant. Any standards may be made from .05 to 1.25 per cent. If the "carbon color" should change on standing, (the change is slight, if any,) all that would be necessary would be to compare it with a standard steel, and thereafter use more or less of the coloring solution, as the case might require. As above stated it is almost impossible to obtain salts which have not absorbed water to a greater or less extent; hence it is necessary for everyone to make up his own "carbon colors" and "iron colors," but this once done and their strength known he can make any desired color at five minutes' notice.

I am still at work on this subject and may possibly be able to give even more satisfactory results.

UNIVERSITY OF MICHIGAN, Dec. 23, 1887.

NOTES ON A NEW OCCURRENCE OF COPPER ARSENATES AND ASSOCIATED MINERALS, IN UTAH.*

BY RICHARD PEARCE.

MY attention has been recently called to a number of rare and beautiful minerals occurring in the Mammoth mine, Tintic district, Utah, and found in the ore shipments from this mine to the Boston and Colorado Smelting Works at Argo. The series is in many respects similar to that from the neighboring American Eagle mine, announced by myself before this Society (C. S. S.) in April 1884,† and subsequently further

* Proceedings of the Colorado Scientific Society, Vol. II, Part II.

† Proc. C. S. S., Vol. I, p. 75.

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investigated by Dr. W. F. Hillebrand,* though the two occurrences are entirely distinct, and the present one contains several species not found in the other.

Enargite is the mother mineral of most of the group, and the paragenetic relations are clearly shown in many of the specimens obtained. The list of recognized species embraces enargite, olivenite, conichalcite, clinoclasite, brochantite, pharmacosiderite, malachite, azurite and several other as yet imperfectly determined ones to be mentioned below.

The identification of the newly recognized minerals rests upon outward resemblances and upon the data to be given, which, though imperfect, are thought to be sufficient to attest to the correctness of the determination of several species either new or of very rare occurrence in this country.

1. *Clinoclasite.*

Occurs, associated with quartz, barite, azurite, malachite, conichalcite and enargite, in groups of stout crystals, with polished blackish blue outer surface, and characteristic bluish green streak. Sp. gr. 4.36, the maximum given by Dana for the species.

Two analyses yielded the following :

	As_2O_5	CuO	HO_2
I	29.36	61.68	7.31
II	28.85	61.22	7.27

Small quantities of Fe_2O_3 and Al_2O_3 were not determined.

2. *Brochantite.*

This mineral occurs sparingly in beautiful, minute, emerald-green crystals, with clinoclasite and pharmacosiderite. One small crystal gave—

CuO	H_2O	SO_3
68.70	12.44	undetermined.

It seems possible that the variety of brochantite called *warringtonite* exists in one of the specimens.

3. *Pharmacosiderite.*

Appears in small yellow cubes, without any tetrahedral

* Ibid., p. 112.

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modifications as far as observed. A chemical examination of 30 mg. gave As_2O_5 31.08 per cent. This is about 9.00 per cent. too low, but the result is propably explained by the amount of inseparable foreign matter in the material tested. In hardness the mineral agrees with pharmacosiderite. The color is somewhat different from any I have before seen in this mineral, some of the crystals having a honey yellow shade. It occurs with clinoclasite and other of the species above mentioned.

4. *Tyrolite?*

A mineral found as a thin coating on quartz with enargite and clinoclasite, has a bright dark green color, with radiate scaly structure. H. about 2.—2.5. It decrepitates violently when heated. 79 mg. of the mineral gave:

As_2O_5	CuO	$Fe_2O_3(Al_2O_3)$	CaO	H_2O	SO_3
27.66	34.00	4.05	10.03	24.26	traces

The presence of CO_2 was not demonstrated beyond a doubt.

Another specimen shows small tabular, flexible, green crystals, lining a cavity in quartz.

H. 1.—2. Only 28 mg. could be obtained for analysis without destroying the entire specimen. I found:

	As_2O_5	CuO	CaO	H_2O
	27.52	37.33	16.00	19.15
Tyrolite (Dana)	25.01	43.88	13.65	17.46

These analyses must be taken for what they are worth. The agreement in arsenic acid and copper oxide seems to indicate that the two substances tested are the same, and the approximate agreement with tyrolite, together with similarity in physical characters, leads me to believe that this rare mineral is present in this series of copper arsenates.

5. *Alteration of Malachite.*

Being somewhat suspicious that the malachite accompanying these arsenates from the Mammoth mine might be found to contain some arsenic acid, I selected a specimen for examination which had all the appearance of malachite and was

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associated with clinoclasite. 108 mg. were carefully freed from all foreign matter and found to contain:

CuO	As_2O_5	Fe_2O_3 (Al_2O_3)	CO_2, H_2O (*by diff.*)
60.50	11.49	4.25	23.76

I had at first thought that the substance might be malachite in process of change to conichalcite, but the entire absence of lime did not confirm this theory.

Regarding the ferric oxide, etc., as accidental impurities and figuring the CuO as 64.75, the substance is found to have very nearly the following atomic ratio:

$$CuO : As_2O_5 : CO_2 : H_2O$$
$$16 : 1 : 7 : 10$$

It would then appear possible, if not probable, that arsenic acid is capable of being substituted for carbonic acid in malachite.

I hope an opportunity will present itself at an early day to enable me to confirm this by an examination of larger quantities of pure material.

ADDITIONAL NOTES ON COPPER ARSENATES AND ASSOCIATED MINERALS FROM UTAH*

By Richard Pearce.

At the last meeting of the Society I partially described a series of minerals from the Mammoth mine, Tintic District, Utah. Since then I have had further opportunities of studying the species then mentioned, and in the new material available have found still other minerals of the same group.

1. *Tyrolite.*

The mineral which I supposed to be tyrolite has been found in larger quantities and in better development than the first examined.

A chemical analysis of 200 mg. of carefully selected material gave—

* Proceedings of the Colorado Scientific Society, Vol. II, Part II.

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CuO	As_2O_5	CaO	$Fe_2O_3(Al_2O_3)$	SO_3	H_2O
42.60	27.87	9.10	0.97	2.45	16.23

If we regard the sulphuric acid to be in combination with lime, and exclude this, together with the ferric oxide and alumina as impurities, we have the following percentage composition for the remainder :

CuO	CaO	As_2O_5	H_2O	*Total*
45.30	7.70	29.60	17.40	100.00

which yields the ratio :

CuO	:	CaO	:	As_2O_5	:	H_2O
9	:	2	:	2	:	16

From these figures it would seem that the mineral in question differs somewhat from the tyrolite of the text-books in having no carbonic acid, though it is by no means proven that this is an essential constituent of the mineral in any instance.

2. *Erinite.*

A mineral found during the past month is thought to be erinite, as it agrees in chemical composition and physical character with that rare species. It occurs as a crystalline coating of dark green color associated with clinoclasite and olivenite. 132 mg. of the substance gave :

	CuO	CaO	Fe_2O_3	As_2O_5	SO_3	H_2O
I. . . .	56.56	0.43	0.85	32.07	trace	6.86
II. . . .	57.43			32.54		7.67

The second analysis figured to 100. gives the following—

CuO	As_2O_5	H_2O
58.82	33.32	7.86

This gives a ratio very near to :

CuO	As_2O	H_2O
5	1	3

which agrees quite closely with that of ermite. The species is a rare one, having until now been found in but a single locality, in Cornwall.

3. *New Mineral.*

Associated with the other arsenates from the Mammoth

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mine is a mineral occurring in most delicate tufts of fine hair-like needles, having a pale green or whitish color. These tufts appear in small cavities, and have a beautiful silky lustre. Only 48 mg. could be obtained for chemical analysis, and this contained some foreign matter, chiefly ochreous oxide of iron, entangled in the delicate fibres so intimately that it could not be entirely separated. The analysis is as follows :

CuO	*CaO*	As_2O_5	H_2O	
50.50	3.19	27.50	12.55	93.74

The Fe_2O_3 and some Al_2O_3 known to be present were lost, together with a little insoluble matter. These impurities would no doubt have brought the total of the analysis nearly to 100. The constituents given may be taken as representing the composition of the mineral, and these calculated on the basis of 100 become

	CuO	*CaO*	As_2O_5	H_2O
	53.87	3.40	29.33	13.40
Calculated	54.40	3.48	28.65	13.45

This gives very nearly the ratio :

CuO	:	*CaO*	:	As_2O_5	:	H_2O
11	:	1	:	2	:	12

from which the formula $6(Cu,Ca)O.\ As_2O_5,\ 6H_2O$ requiring the calculated percentages given above.

I have not been able to find any described mineral corresponding to the above, and should its composition be expressed by the analysis given, I am inclined to believe that the species is new to science.

4. *Chalcophyllite.*

Another mineral lately observed in association with those already described seems to agree in outward appearance with the copper-mica, chalcophyllite. As yet it has been found in too small quantity to afford material for chemical analysis. The mineral occurs in apparently hexagonal or possibly orthorhombic plates of pale apple green color, approaching to emerald green in the thicker tablets. It is readily distinguished

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from tyrolite by the color, though the tubular form of the crystals is nearly the same.

Discussion. Mr. Whitman Cross stated, that at the request of Mr. Pearce, he had made a microscopic examination of the supposed new mineral and had also considered the question of its chemical composition. The needles are very slender, with a length of more than 1 mm. in some cases, by a thickness of less than 0.05 mm. They are deeply striated vertically, and the crystal system could not be determined, although the extinction in polarized light makes a reference to the tetragonal, the hexagonal, or the rhomble system necessary. The index of refraction is high. Pleochroism distinct, the colors observed being, for the thicker crystals, a (and b) sea green, c sky blue.

In regard to the chemical composition, but little could be said at present, but it was considered worthy of note that if Mr. Pearce's formula be correct, and one-half the water be assumed as basic, the mineral would appear to be hydrate of the clinoclasite molecule. Thus

$$6RO, As_2O_5 + 6H_2O =$$
$$2(ROH)_3 As_2O_4 + 3H_2O, \text{ or}$$
$$(ROH)_3 AsO_4 + 1\tfrac{1}{2}H_2O, \text{ while clinoclasite}$$

is $(ROH)_3 AsO_4$ according to the tables of Prof. Groth.

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AN IMPROVED STAND FOR ELECTROLYSIS.

By William Hale Herrick.

The apparatus described by v. Malapert* and noticed in this journal (1, 314) has been improved, and adapted to all kinds of electrolytic determinations, for use in the Laboratory of the

*Ztschr. anal. Chem., 26, 56.

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Pennsylvania State College. Figs. 1 and 2 show the original apparatus. A single wooden standard A supports the apparatus for several electrolytic determinations, the lower board B carrying the vessels containing the solutions to be electrolyzed, and the upper board C

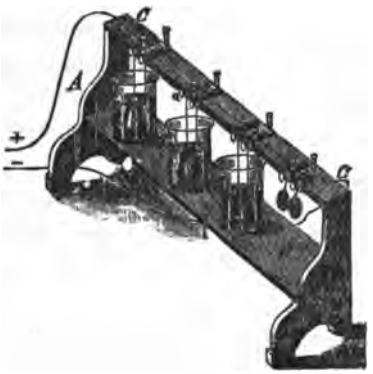

Fig. 1.

Fig. 2.

the apparatus for directing the current as desired. In the apparatus described, the two boards are 18 cm. apart, and the upper board 7 cm. wide.

Fig. 2 shows, on a larger scale, the arrangement for directing the current, connected with each pair of electrodes. The two strips *bb* of brass are 1 cm. wide, 2mm. thick, and their centres 3 cm. apart. The binding-screws *aa* serve for the attachment of the electrodes ; to *cc* are attached the conducting-wires. The switch *d* establishes or breaks connection between the two strips according as it is in the position shown in the cut (closed), or is moved to bear on the curved strip of hard rubber *e* (open).

When the apparatus is arranged, as shown in Fig. 1, with the conducting-wires from the battery connected with the end binding-screws, and adjacent binding-screws throughout connected by wires, the current passes unhindered so long as the switches are closed. To insert any desired number of similar solutions for electrolysis, it is only necessary to place the solutions and electrodes in position, and open the corresponding switches ; the current is then forced to pass through the solutions.

If dissimilar determinations are to be made, the connecting-wires between adjacent pairs of brass strips are removed, and

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the conducting-wires from each battery in use are brought directly to the binding-screws *cc* of one pair of strips.

To remove acid solutions without interrupting the current, v. Malapert uses beakers of heavy glass 8 cm. in diameter and 12 cm. high, with a side tubulure near the top, as shown in Fig. 1. A cork is inserted in the hole between the brass strips shown in Fig. 2, through which passes with little friction a glass tube connected by rubber tubing with a reservoir of water. When the precipitation is complete, a stream of water is turned on, and the acid solution displaced, passing off through the tubulure. A common beaker with siphons can, of course, be used.

A resistance coil of German-silver wire is shown in Fig. 1 connected to the pair of binding-screws at the extreme right.

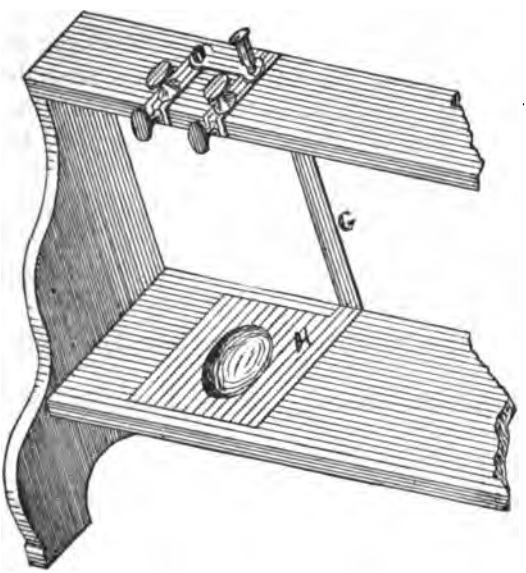

Fig. 3.

Any desired resistance can be thus conveniently inserted.

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The addition shown in Fig. 3 makes the apparatus equally convenient when a platinum dish is used as the negative electrode. The brass strip connected with the negative electrode is extended downward at the rear (G, Fig. 3), to the lower board. Here it is connected with the brass plate H, which is set into the board B so as to be flush with its upper surface, and has a shallow saucer-shaped depression, the centre of which is directly beneath the binding-screw to which is attached the positive electrode. The plate H and the entire strip are cut, in the apparatus in actual use, from a single sheet of brass.

A platinum dish placed in the saucer-shaped depression is firmly supported, and is in good metallic connection with the negative pole of the battery ; the positive electrode is attached as in the original form of the apparatus.

The board B is cut out beneath the plates H, nearly to their full size. This makes it possible, by blocking up the whole apparatus, to warm the solutions, when desirable, by a low flame. (It would perhaps be better to make the side pieces high enough to allow of this.) The brass plate distributes the heat very uniformly.

The apparatus in this form is adapted to all electrolytic uses, is compact, and can be readily made from materials easily obtained. A single stand can be fitted for six solutions, without making it inconveniently large.

The apparatus has given good satisfaction in several months' use.

THE PENNSYLVANIA STATE COLLEGE LABORATORY, Dec. 1887.

COMPOSITION OF DIFFERENT PARTS OF IMPURE SILVER BARS.

BY F. C. BLAKE, MANSFIELD VALLEY, PA.

I present below analyses of samples cut from different parts of impure silver bars, which are of value, though not as complete as I wish, and in the lead determinations not fully reliable. The lead determinations were made by a chemist who

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did not understand the methods necessary to obtain accurate results, and the results could not be checked.

The silver and gold determinations were very carefully made by Mr. G. A. Marsh, the former being from cupellation assays with checks run on each set.

Results A, are upon samples cut from the top of the bars which weighed from 1200 to 1500 ounces, at a a point about one-third of the distance across the bar in both width and length. Results B, are from samples cut from the bottom of the bars at a point similar to that of the top samples. Results C, are from samples cut from the sides at about the center of the bars in depth and about one-third of the length from opposite ends and sides.

Bar No.	*Sample.*	*Silver. per ct.*	*Gold. per ct.*	*Lead. per ct.*	*Copper. per ct.*	*Total.*
1.	A.	26.60	0.120	58.10	14.70	99.50
	B.	27.20	0.107	61.60	11.80	100.70
	C.	27.30	0.100	59.00	11.00	97.40
2.	A.	26.40	0.120	57.50	16.10	100.10
	B.	27.10	0.110	58.80	13.10	99.10
	C.	27.20	0.106	61.10	11.40	99.80
3.	A.	22.90	0.080	68.40	10.70	102.10
	B.	23.30	0.070	66.00	7.00	96.40
	C.	23.10	0.068	68.00	7.80	99.00
4.	A.	23.00	0.080	66.00	8.60	97.70
	B.	23.20	0.070	68.10	7.60	99.00
	C.	23.10	0.087	66.90	7.50	97.60
5.	A.	53.50	0.167	21.40	24.60	99.70
	B.	55.00	0.157	19.50	22.90	97.60
	C.	54.60	0.170	21.40	21.90	98.10
6.	A.	53.60	0.170	20.50	23.30	97.60
	B.	54.60	0.170	21.00	22.50	98.30
	C.	54.40	0.171	21.80	21.40	97.80
7.	A.	59.20	0.220	11.90	28.60	99.90
	B.	60.50	0.192	11.30	26.70	98.70
	C.	60.50	0.220	10.20	26.50	97.40
8.	A.	59.50	0.210	11.70	27.40	98.80
	B.	60.70	0.200	11.60	25.60	98.10

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Bar No.	*Sample.*	*Silver. per ct.*	*Gold. per ct.*	*Lead. per ct.*	*Copper. per ct.*	*Total.*
	C.	60.30	0.227	12.30	26.70	99.50
9.	A.	49.40	0.175	23.70	25.30	98.60
	B.	50.80	0.180	23.30	24.20	98.50
	C.	50.60	0.182	23.10	23.10	97.00
10.	A.	30.60	0.110		17.80	
	B.	32.30	0.103		13.20	
	C.	31.70	0.115		13.30	
11.	A.	31.10	0.110		17.00	
	B.	32.60	0.101		12.10	
	C.	32.50	0.108		12.50	
12.	A.	31.00	0.110		18.90	
	B.	31.40	0.118		14.30	
	C.	31.90	0.115		13.80	
13.	A.	31.10	0.116		17.80	
	B.	32.00	0.115		14.30	
	C.	32.30	0.108		13.60	
14.	A.	33.80	0.145		23.90	
	B.	35.40	0.140		23.80	
	C.	35.00	0.147		23.70	
15.	A.	34.50	0.143		27.40	
	B.	36.00	0.144		23.10	
	C.	36.00	0.143		23.30	
16.	A.	40.40	0.162		27.00	
	B.	41.70	0.158		23.30	
	C.	42.20	0.150		21.30	
17.	A.	39.20	0.152		26.10	
	B.	41.70	0.156		22.90	
	C.	41.40	0.162		21.70	
18.	A.	39.20	0.157		24.60	
	B.	39.90	0.143		19.80	
	C.	40.10	0.146		18.90	
19.	A.	38.70	0.145		24.60	
	B.	40.20	0.137		20.80	
	C.	39.80	0.142		21.30	
20.	A.	41.20	0.153		25.20	
	B.	42.20	0.141		22.50	

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Bar No.	*Sample.*	*Silver. per ct.*	*Gold. per ct.*	*Lead. per ct.*	*Copper. per ct.*	*Total.*
	C.	42.20	0.146		21.00	
21.	A.	41.00	0.155		25.30	
	B.	42.70	0.146		21.50	
	C.	42.60	0.148		21.40	

The bars were tested for bismuth but only a trace was found.

The relative differences in the samples in respect to silver and copper are, as is readily seen, quite irregular.

This irregularity is due not only to the different proportions of lead silver and copper in the bars, but also to the different temperature at which the bars were poured from the melting furnace and the different temperatures of the moulds used.

The first bars poured from a melting show the following average differences:

Silver in bottom	sample	above	top	sample	. . 1.12	per cent.
" side	"	"	"		. . 0.94	"
Copper in bottom	"	below	"		. . 2.6	"
" side	"	"	"		. . 3.2	"

The last bars poured gave:

Silver in bottom	sample	above	top	sample	. . 1.60	per cent.
" side	"	"	"		. . 1.48	"
Copper in bottom	"	below	"		. . 2.7	"
" side	"	"	"		. . 3.3	"

The silver difference in concentration being considerable while the copper is not materially affected.

In respect to the lead and copper proportions the following figures give average results by groups:

Lead between one-half and one-third the copper present:

Silver in bottom	sample	above	top	sample	. . 1.25	per cent.
" side	"	"	"		. . 1.05	"
Copper in bottom	"	below	"		. . 1.8	"
" side	"	"	"		. 1.9	"

Lead and copper about even in per cent.

Silver in bottom	sample	above	top	sample	. . 1.30	per cent.
" side	"	"	"		. . 1.03	"

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Copper in bottom	sample	below	top	sample	. . 1.2	per cent.
" side	"	"	"		. . 1.6	"

Lead between one and one-half and two times the copper:

Silver in bottom	sample	above	top	sample	. . 1.47	per cent.
" side	"	"	"		. . 1.41	"
Copper in bottom	"	below	"		. . 3.3	"
" side	"	"	"		. . 3.9	"

Lead about four times the copper:

Silver in bottom	sample	above	top	sample	. . 1.02	per cent.
" side	"	"	"		. . 1.08	"
Copper in bottom	"	below	"		. . 4.2	"
" side	"	"	"		. . 4.2	"

Lead about eight times the copper:

Silver in bottom	sample	above	top	sample	. . 0.30	per cent.
" side	"	"	"		. . 0.15	"
Copper in bottom	"	below	"		. . 2.3	"
" side	"	"	"		. . 2.0	"

In general the assays of both silver and copper are somewhat lower in the side samples than in the bottom samples. This is to be expected since the bottom of the bar is more quickly chilled and is less affected by the changes in cooling.

The lead seems to undergo less concentration in any part, but I do not consider that the determinations are sufficiently accurate to allow of sharp deductions being drawn.

There seems to be a tendency to a slight gold enrichment of the top samples, but the amount of gold present in the bars is so small that this is not very definitely shown.

I hope at a future time to have results upon bars which have been specially remelted for the experiments and also results upon the interior composition of impure silver bars.

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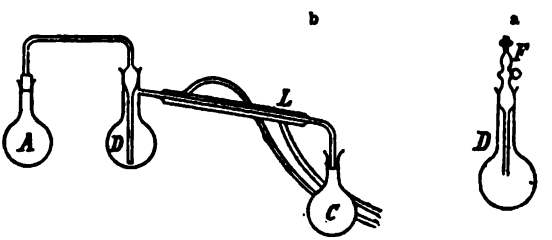
ABSTRACTS.

APPARATUS AND REAGENTS.

A Delicate Thermometer for Lecture Purposes.—Chem. News **56**, 261. This is an air thermometer with ether as the confining liquid. The bulb has a diameter of 17 mm. and a length of 130 mm. This bulb is half filled with ether and the remaining upper half with air. The stem has a diameter of 2.8 mm. and a length of 700 mm. It is melted into the bulb so as to reach its bottom, dipping into the ether. The upper part of the stem is expanded into a bulb to prevent ejection of the ether. In order to make the column of liquid more easily visible a little absolute alcohol is added to the ether, so that some aniline red can be dissolved in it. Change of barometric pressure of course affects the readings, as in an ordinary air thermometer.

Improved Apparatus for the Separation of Iodine, Bromine and Chlorine.—M. Dechan Jour. Chem. Soc. 1887, 690. An improvement upon the apparatus already described for this



purpose (Ibid. 1886, 682) in which ground joints are substituted for those made of cork and rubber. The apparatus *a* is for conducting the distillation in the ordinary manner. The apparatus *b* is so arranged that steam can be passed from A

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through D ; the latter should have a capacity of about 200 c. c.

Lead as a Reducing Agent.—Fr. Stolba, Chem. Centrbl. **58**, 1240. Lead, under proper conditions, reduces ferric, uranic and stannic compounds like zinc, except that in the case of stannic salts only stannous salts are produced—tin not being thrown down when lead is the reducing agent. When iron, for example, is to be reduced to the ferrous state concentrated hydrochloric acid and 2 gms. common salt is added and sheets of thin lead dropped in the solution which is heated to boiling for a short time. 10 gms. $MgSO_4$ is then added and the solution titrated with permanganate.

A New Apparatus for Detecting Very Small Quantities of CO_2 and Other Gaseous Bodies.—O. Rössler, Ber. **20**, 2629. This improved apparatus consists of two glass tubes. One end of the first is drawn out to capillary dimensions and bent upwards to a distance of 1 cm. The second tube is made into a capillary funnel and fits into the throat of the first making an air-tight joint. The point of this funnel is about 1.5—2. cm. from the bottom of the first tube. The substance to be analyzed is placed in the bottom of the bent tube. The funnel is filled with $Ba(OH)_2$ and put in place. On the point of the funnel a drop of $Ba(OH)_2$ will be formed. The lower part of the apparatus is then dipped into hydrochloric acid which, flowing in the bent tube, liberates the CO_2 and causes turbidity in the drop of $Ba(OH)_2$. Since none of the CO_2 escapes, as small an amount as 0.02 mg. has been detected.

This apparatus works equally as well with other gases. For detecting SO_2 replace the $Ba(OH)_2$ by iodide of starch ; for nitric acid, fill the funnel with ferrous sulphate solution, mix the nitrate with sodium chloride and add concentrated sulphuric acid ; for nitrous acid, use potassium iodide solution in the funnel ; for H_2S, use lead acetate ; for NH_3, use copper sulphate, and in like manner other gases may be treated.

S. C.

A New Extraction Apparatus.—Rud. Rempel, Chem. Ztg.

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11, 936, has invented a new extraction apparatus which is shown in the following cut: *A* is the vessel which contains the substance to be extracted; in the bottom of this the tube *D* is fastened by means of a perforated cork. The tube *D* is made with openings at *F* and also near the bottom. Inside the tube *D* another tube *e* is secured in the manner just described and it is notched at *G*; this notch is placed so as to be directly over the point on the opposite end of the tube. The enlarged part of the extractor at *H* is filled with cotton or other suitable filtering material. An inverted condenser *C* is placed at the top of the extractor, with a wad of cotton *K* in the upper end to prevent the circulation of air. The material to be extracted is placed in *A* and the solvent in *B*. On the application of heat the vapors from the latter are driven through the tube *e* and the openings at F, into the condenser, where they are condensed and flow back through the material to be extracted, into the openings at the bottom of tube *D*, into the tube *e* at *G*, and then back into the flask *B*. Since the fluid will rise in *a* as high as the tube *e* the height of the fluid in *a* may be easily regulated by simply moving the tube *e* up or. down. In case the solvent filters very slowly through the material to be extracted, the tube *e* may be omitted entirely without danger of the latter being uncovered by the solvent.

When the extraction is completed the material in the extractor is removed, and by pushing the tube *e* up as far as possible, the solvent may be distilled into the extractor from which it may be withdrawn for future use, thus avoiding separate distilling arrangements. S. C.

Apparatus for Fractional Distillation.—P. Monnet, Monit.

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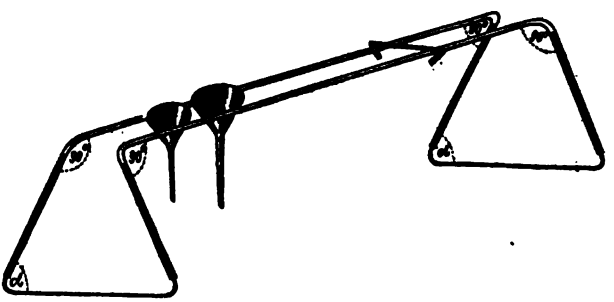
Scient. [4] 1, 335. The apparatus consists of a tube 0.35 to 0.4 m. long and 28–35 mm. internal diameter. This tube is drawn out below to a tube having a diameter of 5 mm. which passes through the cork of the distilling flask. Near the top a side tube is let in which is connected with the condenser. The large tube is filled with shot, pieces of glass or metal. [The writer used such an apparatus several years since; but found it much inferior to the Le Bel-Henninger form and, therefore, did not describe it. Arendt. states (Chem. Central-Blatt. [3] **18**, 1070) that this apparatus has already been described by Hempel. E. H.]

Stand for Holding Filters.—V. Meurer, Ztschr. anal. Chem. **26**, 614. The apparatus shown in the accompanying cut needs little explanation. The two supports, made of bent glass tubes are supported on bent wires thrust in at either end. The tubes are kept from spreading by means of the small rider made of glass rod bent at both ends.



Extraction Apparatus.—R. Schütze, Chem. Zeit. **11**, 1159. This apparatus is intended for extracting small quantities of liquid with a minimum amount of solvent and with the least possible loss. The three way cock can be turned in either of three positions; in position *A* the vessels communicate; in position *B* both vessels are closed; in position *Γ* either vessel is brought into communication with the air. The tubulures are lipped as shown in the cut and the stoppers channeled slightly near the point, so that in one position a small opening is left through which air can pass. If we suppose a liquid is to be extracted with chloroform, the extraction is carried out as follows: The three way cock being in position *B*, the

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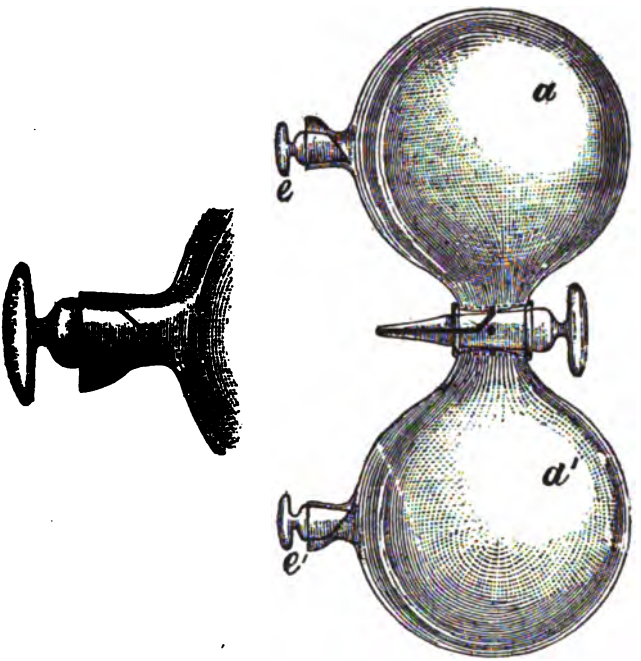
liquid with the chloroform is introduced into either vessel, *a*



for example, and after shaking is allowed to stand until separation takes place. The stoppers *e* and *e'* are then turned so as to communicate with the air and the three way cock brought into position *A*. The chloroform then runs into *a*, and the stop cock having again been brought to position *B*, more chloroform can be poured into *a* and the extraction repeated as often as may be thought necessary. The vessels may be emptied either through e and é, or by bringing the three way cock into position *Γ*.

The Absorption of Carbon Monoxide by Cuprous Chloride.—H. Drehschmidt Ber. **20**, 2752. Hempel has noticed* that in absorbing carbon monoxide with cuprous chloride an increase of volume sometimes takes place. He supposes that this is due to ethylene previously absorbed and now liberated again. The author finds, however, that it is caused by car-

* Ber. 20, 2344.

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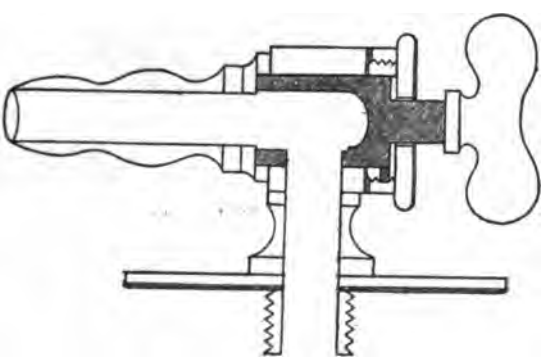
bon monoxide previously absorbed and again liberated, and that it is only noticeable when the amount of carbon monoxide is small in the gas under examination. The amount of gas given up from a saturated solution to an inert gas depends upon its volume—85 c. c. hydrogen increased in volume 3.05 c. c. while 42.5 c. c. increased 1.45 c. c. In case a hydrochloric acid solution of cuprous chloride is used it makes no difference how long the interval between successive absorptions; but with the ammoniacal solution recommended by Hempel, oxidation of the CO to CO_2 slowly takes place with deposition of a layer of metallic copper. Consequently, after 16 hours the CO has almost entirely disappeared. The author, therefore, prefers Hempel's solution for the absorption of CO in the analysis of gases; such a solution which gave up 1.25 c. c. CO to 85 c. c. hydrogen immediately after the absorption of the CO, gave only .10 c. c. to the same volume of gas after standing 16 hours.

Modifications of Gas Lamps and Stopcocks.—H. Schiff, Ztschr. anal. Chem. **26**, 612. The lamps described by Schiff are made almost exactly like the one described by Venable (this Journal **I**, 311.) but are intended for use with ordinary coal gas only. The stop cock, for connecting burners with the gas supply, is shown in the cut and needs no explanation. The total height above the table is only 3 cm.



To File Glass Vessels.—H. Bornträger, Rep. anal. Chem. **7**, 741. A file is dipped in strong caustic soda solution and then in coarse sand. The file covered with the mixture of sand and caustic soda cuts the glass rapidly, without danger of cracking the vessel.

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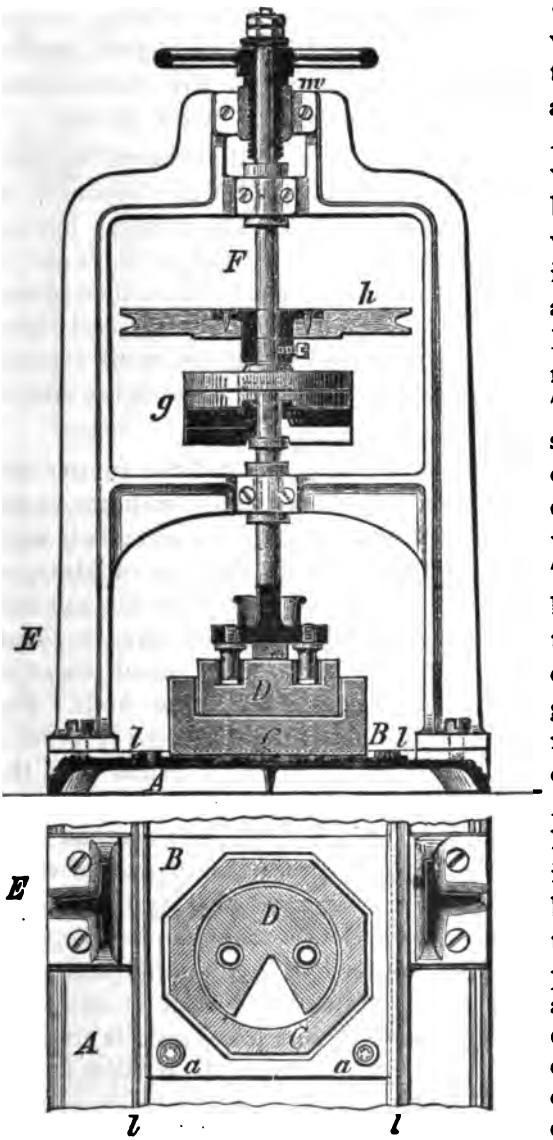
A Mineral Mill.—Karl Zulkowsky, Ber. **20**, 2664. *A* a ground plate with two ledges *ll*. *B* a brass plate which may be shoved in and out and secured by two clamp screws *aa*. *C* the lower stone, which is fastened to the brass plate and hollowed out. *D*, the runner, which has two boxed holes in which the extremities of the mill's axis are placed. Both *C* and *D* are made of agate. The runner has a sector-formed part cut out, the under edge around which is rounded. The rounded edge being on the right, the runner, whose diameter is 1 dcm. goes from left to right, as the hands of a watch travel. *E* is the frame, halfway up which is a beam on which both neck plates of the mill's axis are placed. *F* is the axis, which has a cup on the lower end to collect the oil which drips down. On the axis



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are four notched flat plates to regulate the pressure. Further up at *h*, a wooden pulley is placed.

On the top of the axis is a handwheel. The power applied is from a water motor. A water pressure of two or three atmospheres is sufficient. The water is led through gutta percha pipes which will withstand a pressure of five atmospheres. The weight of the mill is 22 kilos. and its height 52 cm.

Before using, the stones are ground so that they fit together perfectly. A mixture of fine emery and water is poured on them and used to accomplish this end. The mineral having been pulverized in a hand mortar, so that the particles are no larger than grains of sand, about 10 gms. of it are then placed in the cut out part of the runner, and the axis is raised about 1 cm. Then the runner is pressed down and the motor started. Two weights will be sufficient at first, but towards the end all four must be used.

Every ten minutes the mill is stopped and the runner adjusted as at first. It is also well every twenty minutes to entirely lift up the runner, brush off the powder and mix it with that in the lower stone. By this means 10 gms. of MnO_2 in one hour were ground so fine that solution in oxalic and sulphuric acids left no residue. Hard manganese ore, clay-iron stone, and minerals of equal hardness can in quantities of 10 gms. be reduced to an impalpable powder in one hour. For chrome iron stone, add water to the powder until it forms a thin paste. The wet treatment gives better results than the dry. Where the use of water would injure the subsequent determination, either the dry method, or the wet method with absolute alcohol or some volatile hydrocarbon in place of water must be used. The writer experimented with syenite in place of agate, and found that some minerals, for example, spiegeleisen, not easily reduced to powder by the smooth agate, were readily pulverized when the roughened syenite stones were employed. In most cases, however, he found syenite too soft.

A. H. WELLES.

New Mercury Air Pump.—A. Johannis, Ann. chem. phys.

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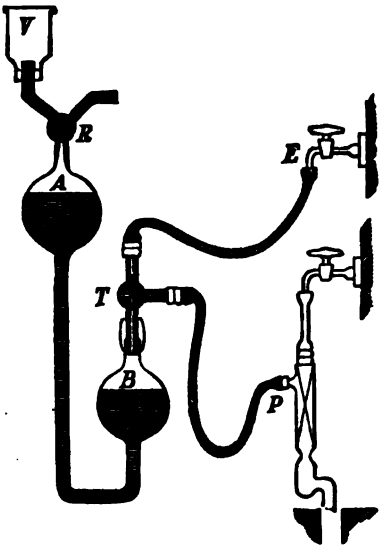
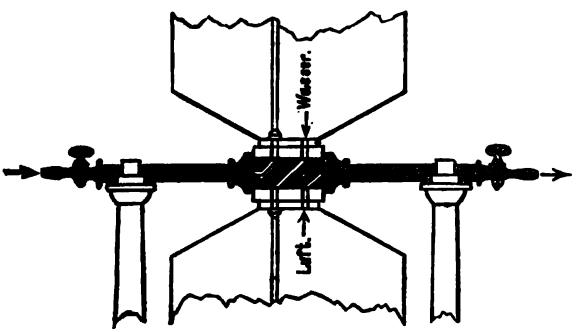
[6] 11, 285. The stop-cock *R* is so bored that the perforation forms one side of an equilateral triangle inscribed in the cross section of the stop-cock. The tubes are joined so that they make with each other angles of 120°, and any two of them can be put in communication by turning the tap. The perpendicular distance between the centres of *A* and *B* is 30 cm. and the tube joining them has a width of 15 mm. By turning the three-way tap T either water is admitted to *B* from E, driving the mercury into *A*, or water or air is pumped out through *P*. The vessel to be exhausted is connected with the tube to the right of *R*. *V* is a sort of mercury trough. This apparatus permits of the exhaustion of a vessel without any moving of the mercury vessel, all that is necessary being the turning of *T* and *R*.



A Double Aspirator.—Schiff and Marangoni, Ztschr. anal. Chem. **26**, 331. The taps are constructed on the system of



Greiner and Friederichs, the axis remains stationary, the cylinders rotating.

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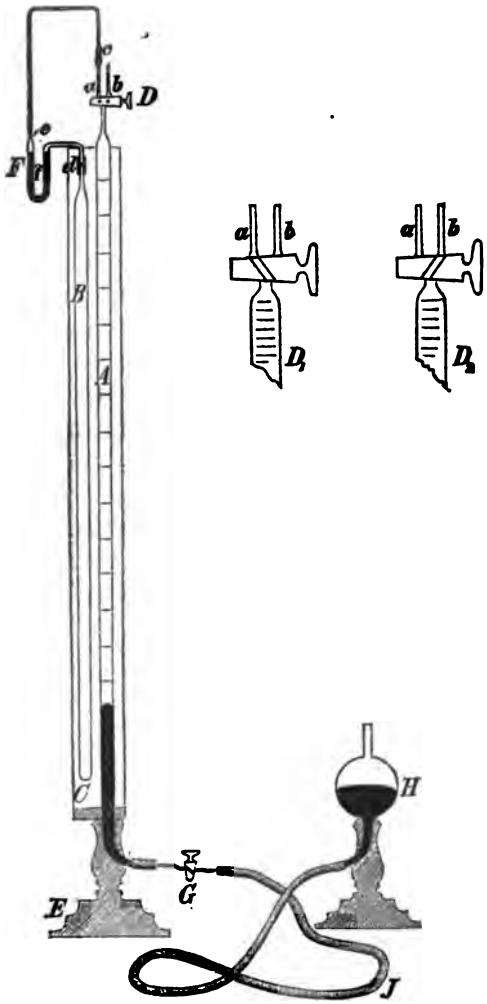
A Gas Burette which is Independent of Variations in the Temperature and Pressure.—W. Hempel, Ber. **20**, 2340. *A* is a gas burette holding 100 c. c., closed at the top by means of a Greiner and Friederich's three way cock *D* and connected below by means of the cock *G* and the rubber tube *J* with the movable bulb *H* containing mercury. *F* is a manometer tube, connected to *A* by the capillary tube *e c*, and to the closed tube *B*. The tubes *A* and *B* are inclosed in the tube *C* and surrounded with water.



The size of the space *e c* is first ascertained as follows: Any amount of air is drawn into the burette (stop-cock in position D_2) and the stop-cock placed in D_1. By raising or lowering *H* the mercury is brought to the same level in the two legs of the manometer tube and the cock *G* being then closed the volume of gas is read off. The bulb *H* is now lowered until the mercury in the manometer tube rises to *c*, the cock *D* is then turned

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half around and the mercury being brought to the same level in *H* and *A* the volume is again read off. The difference between this reading and the first one gives the volume of *e c*.

The measurement of a gas is carried out as follows: The tube *A* is first filled with mercury by raising the reservoir and the gas is then drawn in through *b*, the stop-cock being in position D_2. The stop-cock is then turned to position D_1 and the reservoir raised or lowered until the mercury in the legs of the manometer tube stand at the same height. The volume is then read off and the bulk of gas contained in *e c* added which gives the correct reading. The absorptions are conducted in gas pipettes which are connected with *b* by capillary tubes. If the gases are to be measured moist a drop of water is placed in *B*. Water saturated with the gases to be measured may also be employed as the liquid instead of mercury.

Apparatus for preparing Sulphurous, Carbonic and Phosphoric Anhydrides.—H. N. Warren, Chem. News, **56**, 245. This consists of a large three-neck Wolff bottle. The central opening is fitted with a wide tube passing into the bottle, over a saucer resting on the bottom. Through this opening pieces of sulphur, charcoal or phosphorus are dropped, ignited (by means of a hot wire in case of sulphur or phosphorus), and a current of air passed over the burning material, in at one tubulure and out at the other. From 2–3 lbs. of sodium carbonate may be saturated with SO_2 in less than half an hour with this apparatus. When phosphorus is to be burned the current of air must be slow to avoid cracking the bottle.

The Amount of Moisture left in a Gas after Drying with Phosphorus Pentoxide.—E. W. Morley, Am. J. Sci. [3] **34**, 199. By a method similar in principle to that used by the author in the case of sulphuric acid (Ibid. **30** 141) it is found that "the moisture left unabsorbed by phosphorus pentoxide, if capable of determination, may be very roughly stated as possibly a fourth of a milligram in 10,000 liters." The author has already shown, in the paper quoted, that the amount left

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unabsorbed by sulphuric acid is not far from a fourth of a milligram in 100 liters.

INORGANIC ANALYSIS.

Estimation of Boracic Acid by Gooch's Method.*—Penfield and Sperry, Am. J. Sci. [3] **34**, 222. "The boracic acid in our experiments was set free by nitric acid, distilled over with methyl alcohol and evaporated with a weighed quantity of ignited calcium oxide. Without the use of very large platinum crucibles the evaporation of the boric ether with slaked lime is attended with some difficulty. The calcium borate together with the excess of lime form as a thick crystalline precipitate at the bottom of the crucible and if the methyl alcohol boils during the evaporation some of the precipitate will be carried mechanically out of the crucible; then too the very strong ignition of the CaO necessary to bring it to a constant weight is not so readily accomplished if the crucibles are very large. The following method was found to give very good satisfaction and can be used by any one having an ordinary sized platinum crucible and preferably a platinum dish. The lime after being ignited to a constant weight and slaked is transferred to a large platinum dish and warmed with water till it becomes of a milky consistency; it is not necessary to remove all the lime from the crucible, the latter being put away and used later on. Strong ammonia is poured into the receiving flask of the distilling apparatus described by Gooch, and after conducting the distillation as directed the contents of the receiver are poured into the platinum dish containing the slaked lime, water being freely used in rinsing out the receiver. The dish is then placed on a triangle over the water bath or otherwise gently heated till the volatile products, methyl alcohol and ammonia, are driven off, which by boiling might cause mechanical loss. When these are removed the contents of the dish can be evaporated to dryness. The dried

* See this Journal, 1, 186.

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calcium borate and the excess of lime are now transferred to the crucible in which the lime was weighed, this being easily accomplished by moistening the contents of the dish with water and shoving the bulk of the precipitate into the crucible with a spatula, by rinsing with a little water and by using a rubber on the end of a glass rod all but a very little of the borate and lime can be transferred to the crucible; that which sticks too firmly to the dish can be dissolved in one or two drops of dilute nitric acid which is brought in contact with all parts of the dish with the rubber; the solution is then transferred and rinsed into the crucible. The transfer and washing can readily be made by using not over 30 c. c. of water which can be contained in an ordinary student's crucible. The evaporation from this point goes on very simply, the borate drying out nicely on the water-bath. By placing the platinum crucible in a large porcelain one and gradually raising the heat to strong ignition the borate may be further dried out without any danger of snapping. The residue is finally ignited over the blast lamp till a constant weight is obtained.

In slaking the lime we have found it convenient not to add the water directly to the ignited lime, causing danger from excessive heating and mechanical loss, but to place the open crucible on a watch glass containing water and covered with a bell jar: in this way the lime soon slakes and in case of special hurry hot water may be placed in the watch-glass from time to time so that the atmosphere under the bell jar will be thoroughly saturated; in this way the lime will become so thoroughly slaked in one or two hours that there will be no danger of excessive heating on further addition of water.

The following results were obtained using in all cases about one gram of crystallized borax and one gram of lime: B_2O_3 in borax 36.55, 36.42, 36.58, 36.64, calculated 36.64 per cent."

The Analysis of Alum Cake.—Rowland Williams, Chem. News, **56**, 194. The author, who has had considerable experience in the analysis of alum cake, proceeds as follows: A

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large, representative sample, say 25 gms. (400 grains) is dissolved and filtered through a weighed filter, the insoluble portion being dried and weighed. The filtrate is diluted to 650 c. c. (10,000 grains) and an aliquot portion taken for the estimation of alumina. This may be determined, either by precipitation with ammonia, using the ordinary precautions, or by precipitation with sodium thiosulphate. The first method gives high results, owing to the retention of sulphuric acid by the alumina, even when strongly ignited. By this process the iron is precipitated with the alumina and must afterwards be estimated and subtracted. The thiosulphate method gives accurate results and throws down alumina only mixed with some sulphur, the iron remaining in solution. The thiosulphate method is carried out as follows: The alum solution is first neutralized, if necessary, with sodium carbonate in a porcelain dish, a considerable amount of sodium thiosulphate added and the solution boiled for some time. The precipitate is then filtered off, washed, dried and ignited in the usual manner. The precipitate filters more readily than when thrown down with ammonia [perhaps because of the admixed sulphur]. The precipitated sulphur is entirely driven off by ignition. Iron lime and magnesia may be determined in the filtrate after decomposing the excess of thiosulphate with hydrochloric acid. When potassa and soda are to be determined the alumina must be precipitated by ammonia. The total sulphuric acid is estimated by precipitation with barium chloride in the usual way. The free sulphuric acid may be determined by either of two methods. First, by treating 25 gms. of the powdered sample with strong alcohol in a stoppered bottle, allowing to stand over night, filtering, washing with strong alcohol, adding phenolphtalein to the filtrate and titrating with seminormal or decinormal caustic soda. The addition of water to the alcohol with subsequent evaporation, as practiced by some chemists, is unnecessary and causes loss of sulphuric acid. It is necessary to allow the alcohol to act on the alum cake for at least twelve hours in order to dissolve all of the free sulphuric acid.

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The second method for determining the free sulphuric acid is founded upon the insolubility of quinine, morphine, and strychnine in alum solution free from acid, and the solubility of the sulphates of these alkaloids in the same solution. 65 c. c. (1000 grains) of a clear, 10 per cent. solution of alum cake is poured upon weighed amounts of either of the alkaloids above mentioned. The mixture is stirred frequently for some time, then filtered and the remaining alkaloid washed with cold water, dried and weighed. In calculating the results no allowance has been made for the solubility of the alkaloids in pure aluminous solutions, and the results obtained have consequently been too high. It is assumed in calculating that morphine requires 17.19 per cent. sulphuric acid to form the sulphate, quinine 30.24 per cent. and strychnine 14.67 per cent. The following results were obtained in a comparison of the two methods :

Free Sulphuric Acid.

Alcohol.	*Strychnine.*	*Quinine.*	*Morphine.*
0.41 per ct.	0.54 per ct.	0.50 per ct.	0.51 per ct.

The author thinks that "on the whole it [the alcohol method] yields the most accurate results."

Analysis of Fluoride of Antimony and Sodium.—G. Stein Chem. Zeit. **11**, 1298. This substance (SbF_3. NaF) containing 66 per cent. of Sb_2O_3 has been used lately, in large quantities, as a substitute for tartar emetic. It may be examined as follows :

Qualitative Analysis.—No iron reaction should be obtained on adding potassium ferrocyanide to the solution, and barium chloride should give no precipitate of barium sulphate.

Quantitative Analysis.—0.5 gm. of the double fluoride is dissolved in water, phenol-phtalein added and the solution titrated with ammonia ; the precipitate of antimony oxide is decanted three times, brought upon a weighed filter, dried at 110° and weighed.

Iodometric Studies—G. Topf, Ztschr. anal. Chem, **26**, 137. It is best to titrate iodine with thiosulphate until the color of the iodide of starch disappears, in all cases, and not to

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invert the process. Carried out in this way there is no danger of decomposition of the thiosulphate by the acid added. In cases where thiosulphate must be titrated with iodine solution it is best to add an excess and titrate back the excess with sodium thiosulphate solution.

Starch Solution.—The author prefers a starch solution made according to Zulkowsky's method by heating 1 kilo. of glycerine and 60 gms. potato starch to 190° for one-half hour. To this solution twice its volume of 10 to 20 per cent. salt solution is added.

Standardizing the Thiosulphate.—Iodine has the disadvantage that a brown smeary substance is formed around the stoppers, arising from the action of iodine on dust, which finally covers the inner wall of the bottle. After this has taken place the iodine is no longer fit for use even if it be first heated to melting. Volhard and others have proposed to use a standard solution of potassium dichromate and mix a given amount of this with potassium iodide. This objected to because according to Zulkowsky the reaction between potassium dichromate and potassium iodide is incomplete, and because the solution has an undesirable green color at the finish. The author prefers a solution of potassium iodate or bromate. In order to prevent fungous growths in this solution some common salt should be added.

Standardizing the Iodine Solution.—This may be titrated against pure dry sodium thiosulphate. The thiosulphate is dried in a dessicator, over sulphuric acid. This loses its water of crystallization completely by standing over sulphuric acid for one or two days.

Keeping Properties of Thiosulphate Solutions.—The author concludes as the result of extended experiments that the alteration of sodium thiosulphate solution is caused by: 1, carbonic acid in combination with oxygen; 2, direct sunlight, probably because the solution is warmed while in contact with oxygen and traces of carbonic acid; 3, probably also by organisms present. The precautions needed in making and keeping such a solution are: Preparation with pure water, pre-

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viously boiled to free it from air and carbon dioxide; 2, keeping in a cool place away from direct sunlight; 3, the addition of a small amount of potassium carbonate. If this is added it is necessary to titrate with an acidified iodine solution. An addition of ammonium carbonate, as recommended by Mohr, is not desirable. 4, the author recommends that the solution be covered with light petroleum to exclude the air as far as possible.

Influence of Various Substances upon the Iodide of Starch Reaction.—With water alone more iodine is required to give the iodide of starch reaction the greater the dilution. With sodium potassium and lithium carbonates the amount of iodine required before the color appears is nearly the same for equivalent quantities. Ammonium carbonate absorbs much less iodine, still less is taken up by commercial ammonium carbonate, and sodium and potassium bicarbonates and calcium carbonate are without influence. The action of solutions of barium, calcium, magnesium and zinc chloride solutions, to which either potassium, sodium or ammonium carbonate have been added, is as follows : If we consider the precipitates produced to have the same relative action then with potassium carbonate less absorption of iodine occurs than with either of the other carbonates. Of the chlorides named magnesium absorbs most iodine, and then follow calcium zinc and barium, about in the order named.

Influence of certain additions upon the Iodine-Thiosulphate Reaction.—With neutral solutions addition of ammonium carbonate causes an absorption of iodine which is not entirely liberated again when the solution is acidified. The same is true of sodium barium and calcium hydroxides, the same is true of potassium sodium, and lithium carbonates ; bicarbonates of sodium and potassium cause a slight absorption of iodine even when an excess of carbonic acid is present. Ammonia, as might be expected, absorbs a considerable amount of iodine as nitrogen iodide. Barium, calcium, magnesium and zinc carbonates, and magnesium and zinc hydroxides cause a small absorption of iodine, aluminum hydroxide is entirely without

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influence. This absorption of iodine is caused by the formation of hypoiodates which oxidize the tetrathionate to sulphate in alkaline solution.

In a "Special Part" (Ibid p. 277) Topf. has also studied the action of sulphuric acid on potassium iodide. He finds that sulphurous acid is only produced when the solutions are concentrated. Bunsen states that the reason concentrated sulphurous acid solutions are not oxidized completely by iodine is that sulphuric acid is formed and the reverse reaction takes place. According to the above experiments, however, this is not the case, and another explanation must be sought. [This has been found by Volhard, see below.]

Volhard (Ann. Chem. **242**, 93) has studied the reaction between iodine solution and sulphurous acid solution. He finds that if the sulphurous acid is run into the iodine it is completely oxidized to sulphuric acid, even when the solution is strong (1.864 per cent SO_2). If, however, the sulphurous acid is in excess, the following, in addition to the normal reaction, occur:

$$\text{I.—}SO_2 + 4HI = S + 2H_2O + 4I$$
$$\text{II.—}2SO_2 + 4H_2O + 4I = 2H_2SO_4 + 4HI$$
$$\text{III.—}3SO_2 + 2H_2O + 4HI = 2H_2SO_4 + S + 4HI$$

In making titrations, therefore, the sulphurous acid should always be run into the iodine solution until this is decolorized, then starch added and iodine run in from a small hand pipette until the blue color makes its appearance.

Salzer (Chem. Zeit. **11**, 754) also makes some remarks upon this subject which seem of little importance in view of Volhard's more complete examination of the subject.

Separation of Sulphuric and Tetrathionic Acids.—G. Topf, Ztschr. anal. Chem. **26**, 166. To effect a good separation of sulphuric acid from tetrathionic, it is necessary to add the barium chloride to a neutral or faintly alkaline solution in the cold, and to filter as soon as the barium sulphate settles.

The Estimation of Lithium as Sulphate.—C. Gottig Ber. **20**, 2914. When lithium is estimated as sulphate, by heat-

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ing with excess of sulphuric acid, it is necessary to heat at a red heat to a constant weight. At 340° an acid sulphate is formed which can only be completely decomposed by ignition at a low temperature for several hours. This is contrary to the statement found in a well-known text-book, where it is said that no acid sulphate exists, and only gentle heating is necessary to drive off the excess of acid.

Valuation of Zinc Dust.—G. Topf, Ztschr. anal. Chem. **26**, 286. When zinc dust is mixed with iodine the zinc and iodine combine leaving the oxide of zinc and foreign substances undissolved; the excess of iodine is then estimated with sodium thiosulphate. The iodine is weighed out in the solid form and placed together with 1½ times its weight of potassium iodide and some water, in a stoppered glass flask. The zinc dust is then weighed out from a tube directly into the flask, care being taken that none adheres to the side of the flask. Some pieces of glass are added and the mixture thoroughly mixed by shaking. The pieces of glass help to break up and moisten the zinc dust. The reaction is complete in 20–30 minutes. Any lead present is converted into iodide. Small black particles—probably carbon—and zinc oxide remain undissolved. The best plan is to acidify with dilute, pure acetic or hydrochloric acid, and to estimate the excess of iodine in an aliquot portion of the solution. The following results were obtained:

I	*a* with dichromate*	88.8	per cent. Zn.
	b with iodine	91.7	" " "
	c " "	91.5	" " "
	d " "	92.1	" " "
II	*a* with iodine	91.44	" " "
	b " "	91.46	" " "

The author considers that, for reasons not explained, the dichromate method gives results which are too low.

Determination of Phosphoric Acid in Potable Water.—T. L. Phipson, Chem. News, **56**, 251. Contaminated water always contains phosphoric acid while pure water never con-

* Drewsen's method, Zeit. anal. Chem. **19**, 50.

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tains more than minute traces. The phosphoric acid may be determined as follows: "To about a pint of the water a very small quantity of solution of pure potash alum is added, and then a drop or two of ammonia. Without separating the precipitate the water is rendered distinctly acid by addition of pure acetic acid; the phosphate of alumina remaining is separated, dissolved in nitric acid, and the phosphoric acid determined by the ordinary molybdate test.

Gravimetric Determination of Chlorine.—Fr. Stolba, Chem. Centrbl. **58**, 1240. Where small quantities of chlorine are to be estimated, as in water analysis for example, (less than 80 mg.) the precipitate of silver chloride may be collected on a large Schleicher and Schüll filter, dried and the filter folded so that the precipitate in the point is enclosed in several layers of paper. The filter is then charred very slowly in a covered platinum crucible. If the carbon is then burned off at a low temperature with access of air spongy silver remains behind. The silver is then tested for purity by solution in HNO_3. When the operation is carried out as above the platinum crucible is not attacked in the least degree.

ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

Oxygen.—Keiser, (Ber. **20**, 2323) attempts to ascertain the composition of water directly by weighing hydrogen occluded in palladium, expelling it by heat, and burning it to form weighable water. Three experiments gave results as follows:

	0.65100	grm.	H.	gave	5.81777	grm.	H_2O
	.60517	"	"	"	5.41540	"	"
	.33733	"	"	"	3.00655	"	"
Sum,	1.59350	"	"	"	14.23972	"	"

Hence, in sum, O=15.8722. The separate experiments give respectively 15.8732, 15.8970, and 15.8224; a rather poor concordance. What precautions were taken to avoid obvious sources of error is not stated.

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The Composition of Water by Volume has been reinvestigated by Alexander Scott. (Proc. Roy. Soc., **42**, 396; and Chem. News, **56**, 173.) It is well known that oxygen and hydrogen, *as actually measured at ordinary temperatures and pressures*, do not rigidly conform to Boyle's law. They vary from it in opposite directions; and this fact must be taken into account before we can deduce their relative atomic weights from their relative densities. The author, in his experiments, has paid especial attention to the following points:

1. The preparation of purer gases.
2. The use of larger volumes.
3. The measurement of both gases in the same vessel.
4. The analysis of the residue after explosion, and determination of the impurity in each experiment. In twenty one experiments it was found as a most probable value that 1.994 volumes of hydrogen combine with one volume of oxygen. Hence, if the density of O is 15.9627, its atomic weight becomes 16.01.

Fluorine.—Christenson, (Journ. prakt. Chem., [2] **35**, 551) determines the atomic weight of this element by means of the salt $4NH_4F.Mn_2F_6$. This salt, added to a mixture of potassium iodide and hydrochloric acid, liberates iodine, which may then be titrated with sodium hyposulphite. One molecule of the salt sets free two atoms of iodine. The following data are given:

3.1199 grm.	$(NH_4)_4$	Mn_2F_{10}=	2.12748 grm.	I.
3.9190 "	"		2.6702	"
3.5005 "	"		2.384429	"
1.2727 "	"		.86779	"

Hence, in mean, if H=1, N=14.01, I=126.54, and Mn=55.0;

F=18.94.

Gold.—Krüss, (Ber. **20**, 2365) criticizes the work of Thorpe and Laurie.* He supposes that the potassium gold bromide used by them contained traces of free gold; and, applying

*Jour. Chem. Soc, June, 1887. See this Journal, Vol. 1, No. 3, p. 338.

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corrections to their data, deduces a value for Au closely agreeing with his own.

Thorpe and Laurie, (Ber. **20**, 3036, and Journ. Chem. Soc., Dec. 1887), reply to Krüss, and show that the gold salt employed by them was not contaminated as he supposed.

Mallet, (Chem. News, No. 1452), gives a preliminary notice of a redetermination of the atomic weight of gold now in progress in his laboratory. His results, so far, indicate a slightly higher value for Au than was found by Thorpe and Laurie. His main method consists in measuring the amount of hydrogen evolved during the solution of a known weight of zinc in dilute sulphuric acid, and then the amount of gold precipitate from its solution by another sample of the same zinc. A direct ratio between Au and H is thus obtainable.

Zinc.—Reynold's and Ramsay's paper on the atomic weight of zinc, noticed in No. 3, Vol. 1, of this Journal, has appeared *in extenso* in the Journal of the Chemical Society for December, 1887.

The Determination of Atomic Weights by Means of the Normal Sulphate.—G. H. Bailey, (Jour. Chem. Soc. LI, 676, Aug. 1887) discusses the conditions of accuracy in determinations of atomic weight which depend upon the ignition of sulphates. First, the sulphate must be free from excess of sulphuric acid ; and secondly it must not have begun to decompose. In each case, therefore, a range of temperature must be found between the point at which all free acid is expelled and the point at which decomposition sets in, wide enough to admit of securing constant weight of the pure normal salt. With bismuth sulphate, all free acid is driven out at 345°, and decomposition begins between 405° and 435°. Decomposition, however, is complete only above the fusing point of the residual oxide, which itself is slightly volatile. The latter part vitiates atomic weight determinations involving its ignition. Other experiments are cited concerning the sulphates of zinc, barium, lead, magnesium and didymium.

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IRON AND STEEL.

EDITED BY P. W. SHIMER.

Determination of Phosphoric Acid.—A. A. Blair, in an account of the methods employed for the analysis of iron ores for the tenth census, gives the following sketch of the various methods proposed for the determination of phosphoric acid, and discussion of the methods in general use at the present time:—

"I shall not attempt in this sketch to trace those methods which are not applicable to iron ores, among which may be mentioned the lead, (*b*) mercury, (*b*) uranium, (*c*) and tin (*d*) methods, and that based on the separation and weighing of ferric phosphate and the titration of the iron by solution of permanganate. (*e*)

"The first step toward an accurate method for the estimation of phosphoric acid in presence of iron was taken when Otto, (*f*) in 1844, suggested its precipitation as $Mg_3(NH_4)_2P_2O_8$ by adding magnesic sulphate to an ammoniacal liquid in which the Fe_2O_3 was kept in solution by tartaric acid.

"The separation of this acid from a large excess of ferric oxide was still very difficult, and the results obtained were very inaccurate.

"In 1846 Svanberg & Struve (*g*) discovered the reaction of phosphoric acid with ammonic molydate, and Rose (*h*) confirmed their statements. This, however, was only qualitative.

"R. Weber, (*i*) in 1846, showed the necessity for converting any pyrophosphoric into orthophosphoric acid, and recommended heating with H_2SO_4 to accomplish this result.

"About this time Fresenius (*j*) published the method

b Pogg. Ann., lxxvi, 218.
c Leconte, Compt. Rend., xxix, 55.
d Compt. Rend., xxxiii, 385.
e Raewsky, Compt. Rend., xxiv, 681.
f Ann. d. Pharm., viii, 142, 167.
g Jour. für Pr. Chem., xliv, 291.
h Pogg, Ann., lxxvi, 26.
i Pogg. Ann., lxxiii, 137.
j Jour. für Pr. Chem., xlv, 258.

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which is largely the same as that which is now known as the acetate method. It is in substance as follows: Reduce the iron in the acid solution with Na_2SO_3 until Na_2CO_3 produces a white precipitate; boil off all SO_2, neutralize nearly with Na_2CO_3, add a few drops of chlorine water and excess of sodic acetate; add chlorine water until the liquid is red, boil until it clears, and filter hot. The precipitate contains all the P_2O_5. Dissolve this precipitate in HCl and precipitate the iron by NH_4HO and $(NH_4)_2S$, or precipitate, after reducing with Na_2SO_3, by NaHO, boiling hot, filter, and in the filtrate precipitate with magnesium mixture and ammonia.

"He stated that neither citric acid nor sugar possessed any advantage over tartaric acid in preventing the precipitation of small amounts of iron with the $Mg_2(NH_4)_2P_2O_8$.

"J. C. Nesbitt (*k*) claimed that the precipitate of $Mg_2(NH_4)_2P_2O_8$, from a solution containing $MgSO_4$, NH_4Cl, NH_4HO, Fe_2O_3, and Al_2O_3, contained varying amounts of Fe_2O_3 and Al_2O_3 unless the solution was very dilute and contained a great excess of tartaric acid and ammonia; and Fresenius (*l*) stated that at a certain degree of concentration a precipitate was thrown down from a solution containing only Mg_2SO_4, NH_4Cl, tartaric acid, and ammonia.

"Rose, a little later, published an account of the various methods for the determination of P_2O_5, and said, among other things, in regard to the precipitate of $Mg_2(NH_4)_2P_2O_8$, that the solution, after the addition of $MgSO_4$, NH_4Cl, and NH_4HO, should stand for some hours, and should not be heated above 30°.

"The precipitate should be washed (according to Fresenius) with ammonia water, and the presence of a great excess of ammoniacal and other salts, Rose stated, had no influence upon the precipitation. He added that $(NH_4)_2CO_3$ threw down an insoluble double salt of Mg and NH_4, and should not be used instead of NH_4HO, and also that P_2O_5 could not be perfectly separated from iron by $(NH_4)_2S$, for while the FeS contained no P_2O_5, the filtrate deposited iron with the Mg_2

k Jour. Chem. Soc., i, 44. *l* Jour. Pr. Chem., xlv, 259.

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$(NH_4)_2P_2O_5$. He also suggested the precipitation of P_2O_5 by $BaCO_3$.

"Sonnenschein (*m*) first used, about 1850, the molybdate method quantitatively. He used a solution containing 1 part ammonic molybdate and 20 parts HNO_3. Of this solution he used 30 times as much as was necessary to precipitate the P_2O_5, allowed it to stand several hours at a gentle heat, filtered, washed with the precipitant dissolved on the filter in NH_4HO, and then precipitated by Mg mixture.

"Ullgren, (*n*) about the same time, proposed the following method: A solution of iron ore in HCl, or of the iron in HNO_3, evaporated to a sirupy consistency with HCl and diluted, was poured into a solution of potassic sulphide and potassic silicate (1 gram of iron to 5 grams potassic sulphide and 1 gram potassic silicate). The precipitate contained MgO, CaO, Al_2O_3, and sulphides of positive metals; the filtrate, potassic phosphate, and sulphides of negative metals. The filtrate was mixed with freshly precipitated $PbCO_3$, filtered and washed with water containing one-tenth its volume of a concentrated solution of $(NH_4)_2CO_3$ and NH_4HO. The filtrate was evaporated to dryness, the mass moistened with HCl, diluted, and filtered from SiO_2. Filtrate contained P_2O_5 and traces of Fe_2O_3, etc. Tartaric acid was added, and P_2O_5 precipitated by Mg mixture as usual. He also suggested adding ferrocyanide of potassium and K_2S to the nitric acid solution of the iron containing tartaric acid, ammonia, and magnesic sulphate, filtering off the precipitate of S and $Mg_2(NH_4)_2P_2O_8$, and fusing with Na_2CO_3, and determining P_2O_5 in the filtered solution, after acidulating with HCl, by Mg mixture.

"Kremers (*a*) gave the proper strength of ammonia water for washing the precipitate of $Mg_2(NH_4)_2P_2O_8$ as 3 parts water to 1 part NH_4HO. He said that the precipitate dissolved in all other mixtures.

"W. Wicke (*b*) recommended molybdate of lead instead of molybdate of ammonia as a precipitant of P_2O_5.

m Jour. Pr. Chem., liii, 339.
a Pogg. Ann., lxxxiv. 77.
n Jour. Pr. Chem., liii, 33.
b Ann. Ch. Phar., xcv, 373.

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"W. Knop (*c*) stated that pure silicate of potash treated with HNO_3 and ammonic molybdate gave a precipitate similar to that obtained from a small amount of P_2O_5,

"Damour and H. Sainte-Claire Deville, (*d*) in 1858, showed that oxide of cerium added to an acid solution of P_2O_5 gave a pale yellow precipitate.

"Staedeler (*e*) recommended Otto's method, but suggested redissolving and reprecipitating the first precipitate of $Mg_2(NH_4)_2P_2O_8$.

"A. Lipowitz (*f*) suggested the use of a molybdate solution containing 2 MoO_3, 1 tartaric acid, 15 water, 10 NH_4HO, and 15 HNO_3. After adding the precipitant to the solution of iron containing P_2O_5, he heated it to boiling, and weighed the precipitated phospho-molybdate of ammonia on a counterpoised filter, dried at 20° or 30°, or better, over H_2SO_4. The precipitate contained 3.607 per cent. P_2O_5.

"H. Struve (*g*) dissolved the iron in HNO_3 and HCl, evaporated to dryness, redissolved in HCl, and filtered from SiO_2, precipitated by NH_4HO, fused precipitate with Na_2CO_3, dissolved in hot water, filtered, and determined P_2O_5 in filtrate by Mg mixture.

"V. Eggertz, (*h*) in 1860, recommended the molybdate method. He dissolved MoO_3 in 4 parts NH_4HO, and filtered into 15 parts HNO_3 (1.2 sp. gr.).; dissolved the iron or steel in HNO_3, evaporated to dryness, redissolved in HCl, added molybdate solution, and set it aside at a temperature of 40°, with occasional stirring for 2 or 3 hours. He filtered the dried precipitate at 95°, and weighed. The precipitate contained 3.74 per cent. P_2O_5.

"C. Chancel (*i*) treated the iron ore with HNO_3, precipitated any H_2SO_4 with $BaCl_2$, and HCl with $AgNO_3$; precipitated the Ag and reduced the iron with H_2S, boiled off in current of CO_2, and precipitated P_2O_5 with nitrate of bismuth. The precipitate contained 31.28 per cent. P_2O_5.

"R. Warrington, Jr., (*j*) recommended the use of citric

c Chem. Centr., 1857, 691 and 861.
d Inst., 1858, 69.
e Ann. Ch. Pharm., cix, 306.
f Pogg. Ann., cix, 135.
g Jour. Pr. Chem., lxxix, 321.
h Jour. Pr. Chem., lxxix, 496.
i Compt. Rend., li, 882.
j Jour. Chem. Soc., xvi, 304.

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acid instead of tartaric acid, to avoid precipitation of Mg salts with the $Mg_2(NH_4)_2P_2O_8$.

"Fr. Mohr (*k*) showed that the precipitate in a solution of iron by sodic phosphate had the formula $Fe_2O_3P_2O_5$. On long washing the precipitate was decomposed P_2O_5 and Fe_2O_3, dissolving with an acid reaction.

"Schloessing (*l*) ignited the phosphate in a mixture of SiO_2, then transferred to a carbon boat, and heated in a porcelain tube in a current of CO. The loss of weight was P_2O_5. If the porcelain tube is connected with a silver tube heated to redness and containing Cu, the Cu takes up all the P from its volatile compound ; or if the gas from the porcelain tube is led into a bulb apparatus containing $AgNO_3$ and warmed in a water-bath to 80° or 90° C., the silver phosphide collected here and the red phosphorus remaining in the tube may be oxidized with HNO_3, evaporated to dryness, heated to incipient fusion, extracted with water, and the residue weighed as $3\ Ag_3OP_2O_5$.

"R. Warrington, Jr., (*m*) recommended neutralizing the nitric-acid solution after separation of SiO_2 with NH_4HO, and precipitating with acetate of lead (or with $Pb(NO_3)_2$ and PbO). The lead phosphate, after washing with warm water containing some ammonic acetate, was dissolved in dilute HNO_3 and decomposed with H_2S. From the filtrate, which contained all the P_2O_5 with very little iron, the P_2O_5 was precipitated after the addition of a little critic acid by Mg mixture.

"R. Fresenius (*n*) remarked, in regard to the molybdate method: 1. HNO_3, even in large excess, did not influence the exactness of the method. 2. HCl in large amount prevented partially or entirely, the precipitation of the phospho-molybdate ; 3. 3 per cent. of HCl gave results that were approximate, but still too low. 3. In the presence of much HNO_3, HCl was still more disadvantageous. 4. H_2SO_4, Fe_2Cl_6, Al_2Cl_6, even in large amount, did not influence the result. 5. With much NH_4Cl the results were too low, as they were also when the solution was very dilute.

k Zeit. Anal. Chem., ii, 250.
l Compt. Rend., lix, 384.
m Chem. News, xi.
n Zeit. Anal. Chem., iii, 446.

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"F. Knapp (*o*) and R. Pribram (*p*) claimed that in a solution containing much Al_2O_3 the precipitation of the $Mg_2(NH_4)_2P_2O_8$ in the presence of tartaric acid and ammonia was entirely prevented.

"J. Spiller (*a*) treated the HCl solution with ammonic bisulphite, drove off the excess of SO_2 by heating, cooled the solution to 20°., and added a solution of ammonic carbonate until the precipitate, at first red, became greenish in color. This precipitate, which contained all the P_2O_5, was filtered off and dissolved in HCl, the iron separated according to Fresenius' method by $(NH_4)_2S$ and NH_4HO, and the P_2O_5 precipitated in the filtrate by Mg mixture.

"Brassier (*b*) suggested the use of $MgCl_2$ instead of $MgSO_4$.

"E. G. Tosh (*c*) recommended Spiller's method, but instead of separating the Fe_2O_3 and P_2O_5 by $(NH_4)_2S$ and NH_4HO, added citric acid to the HCl acid solution of the precipitate by ammonic carbonate, and precipitated the P_2O_5 by Mg mixture and ammonia, as $Mg_2(NH_4)_2P_2O_8$.

"Tantin (*d*) proposed treating iron or steel with HCl in a flask, and passing the gases evolved through a solution of KHO to separate S, and then through a solution of nitrate of silver in which the phosphuretted hydrogen precipitates silver as phosphide. This phosphide of silver he filtered off and treated with aqua regia, which oxidized the P to P_2O_5 and rendered the Ag insoluble as chloride. The AgCl he filtered off, and determined the P_2O_5 in the filtrate.

"W. Kübel (*e*) showed that $Mg_2(NH_4)_2P_2O_8$ was much less soluble in ammonia water than Fresenius supposed. As he found basic magnesic sulphate in this precipitate, he recommended re-solution and reprecipitation.

"E. Kessel (*f*) stated that the amount of basic magnesic sulphate precipitated with the $Mg_2(NH_4)_2P_2O_8$ was very small if no great excess of $MgSO_4$ was used and sufficient NH_4Cl. He also claimed that the presence of soluble Mg salts decreased

o Zeit. anal. Chem., 1865.
p Vierteljahrschr. Pr. Pharm., xv, 184.
a Jour. Chem. Soc. (2), iv, 148.
b Ann. Chem. Phys. [4], vii, 355.
c Chem. News, xvi, 168.
d Chem. News, xviii, 252.
e Zeit. anal. Chem., viii, 125.
f Zeit. anal. Chem., viii, 164.

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the solubility of the $Mg_2(NH_4)_2P_2O_8$, and that dilute ammonia dissolved it, the solvent action of this latter being increased by the presence of NH_4Cl.

"Th. Petersen (*g*) restated the necessity for completely removing SiO_2 before precipitating P_2O_5 by molybdate solution.

"F. Kessler (*h*) proposed to determine P in iron and steel by precipitating the Fe from solution by K_4FeCy_6, and in the filtrate determining P_2O_5 as $Mg(NH_4)_2P_2O_8$.

"Meinicke (*i*) suggested dissolving iron or steel in double chloride of copper and ammonium, filtering, and treating the residue with HNO_3, and precipitating P_2O_5 in this solution with molydate solution.

"E. Richters (*j*) recommended washing the precipitate of ammonic phospho-molybdate with solution of ammonic nitrate.

"E. W. Parnell (*k*) showed the insolubility of $Mg_2(NH_4)_2P_2O_8$ in ammoniacal liquids containing excess of Mg salt or sodic phosphate.

"J. Parry (*l*) dissolved iron or steel in aqua regia, and after separating SiO_2 transferred the HCl solution to a flask and added sufficient ammonia to precipitate all the Fe_2O_3, then just enough HNO_3 to dissolve the precipitate. He heated the solution nearly to boiling, and added an excess of an aqueous solution of ammonic molybdate. If there was no precipitate he added HNO_3, drop by drop, shaking the flask constantly until a distinct precipitate appeared, after which he added a small additional amount of HNO_3, shook the flask well, and allowed the precipitate to settle for a few minutes. He filtered, washed with water containing a little HNO_3, and weighed the precipitate of phospho-molybdate of ammonia, which contained 1.63 per cent. of P.

"T. R. Ogilvie (*m*) made a number of experiments to show the effect of varying amounts of Mg salts, citric acid, Al_2O_3, Fe_2O_3, and ammonic oxalate on the precipitation of P_2O_5 as $Mg_2(NH_4)_2P_2O_8$.

g Verhandl. Geolog. Reichsanst., 1869, 80.
h Jour. Pr. Chem. [2], 2, 364.
i Zeit. anal. Chem., 1871, p. 280.
j Zeit. anal. Chem., 1871. 305.
k Chem. News, xxiii, 145.
l Chem. News, xxv, 229.
m Chem. News, xxxi, 274; xxxii, 5, 12, 70.

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"E. W. Parnell (*n*) said, in answer to Ogilvie, that the purity of the precipitate of $Mg_2(NH_4)_2P_2O_8$ was not affected by the quantity of the Mg salts, but by the manner of precipitation. He recommended the use of dilute solutions, and said they should stand quiet for a long time.

W. Flight (*o*) discussed various methods and recommended—

"1. To separate P_2O_5 from Fe_2O_3, he passed H_2S through the weak acid solution, then added $(NH_4)_2S$ in excess, boiled, filtered, washed with H_2S water, and determined P_2O_5 in filtrate.

"2. From Al_2O_3 he added excess of NaHO to solution, then $BaCl_2$ to precipitate all the P_2O_5, allowed to stand several hours protected from CO_2, filtered and washed with NaHO water, decomposed precipitate and determined P_2O_5.

"3. From Fe_2O_3 and Al_2O_3 he treated the not too acid solution with excess of $Na_2S_2O_3$, boiled, filtered P_2O_5 partly with Al_2O_3 in precipitate and partly with FeO in filtrate. He then separated P_2O_5 by methods I and II.

"T. E. Cairns (*p*) showed the inaccuracy of Sonnenschein's molybdate method when the solution was not heated above 40° C., unless it was allowed to stand several days. He recommended dissolving the iron or steel in HCl and $KClO_3$, evaporating to dryness to get rid of SiO_2, precipitating the Fe_2O_3 and P_2O_5 by NH_4HO, filtering, dissolving this precipitate in HNO_3, and evaporating down, diluting to 250 c. c., neutraliizing by NH_4HO, adding 'molybdate solution,' heating nearly to boiling and allowing the phospho-molybdate to settle. He recommended washing this precipitate with "molybdic acid solution", dissolving in NH_4HO, neutralizing by HCl, and precipitating the P_2O_5 by Mg mixture.

"O. Korschelt (*a*) suggested the use of potassic molybdate instead of ammonic molybdate. He prepared the solution by dissolving 1 part MoO_3 in 1 part KHO and 6 parts water, after cooling adding a solution of one-half part tartaric acid in 2 parts water, and finally 7½ parts nitric acid, boiling and filtering

n Chem. News, xxxii, 222.
o Jour. Chem. Soc., xxviii, 592.
p Am. Chemist, vii, 215.
a Dingler's Pol. Jour., ccxxv, 158.

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while hot. He dissolved the iron or steel in the smallest possible amount of boiling nitric acid, filtered, and added the heated solution to an excess of the molybdate solution in a capsule, also heated on the water-bath. He filtered on a balanced filter, washed with dilute HNO_3 and then with alcohol, dried at 120° to 130° C., and weighed. The precipitate contained 1.73 per cent. P.

"Boussingault (*b*) used the fact of the insolubility of phosphate of cerium (pointed out by Damour and Deville) in HNO_3 in the determination of P_2O_5 in iron and steel.

"Finkener (*c*) approved of Sonnenschein's method, and suggested the addition of an increased amount of NH_4NO_3 and the washing of the precipitate with a solution of ammonic nitrate and nitric acid. He washed the precipitate into a weighed crucible, evaporated off the water, heated it over wire-gauze to expel the NH_4NO_3, and weighed the ammonic phospho-molybdate. It contained 3.794 per cent. P_2O_5.

"E. Riley (*d*) recommended most strongly the acetate method, using $MgCl_2$ instead of $MgSO_4$, in the magnesia mixture, and citric acid to keep the Fe_2O_3 in solution. He considered a large amount of citric acid necessary. He allowed the solution to stand over night before stirring, then stirred vigorously, and allowed to stand for 24 hours before filtering off the precipitate of $Mg_2(NH_4)_2P_2O_8$. He suggested, also, a combination of the acetate and molybdate methods by dissolving the acetate precipitate in HCl, adding excess of NH_4HO, acidulating by HNO_3, and precipitating by ammonic molybdate, filtering and weighing the phospho-molybdate of ammonia.

"For the determination of P_2O_5 in iron ores, iron, and steel there are practically but two methods in general use at the present day—the molybdate and the acetate—unless we consider a combination of the two a separate method. Each has its ardent admirers, but the general opinion among chemists of experience is, that either method will give accurate results

b Dingler's Pol. Jour., ccxxv, 158.
c Deut. Chem. Ges. Ber., 10, pp. 1638-1641.
d Chem. Soc. Jour., 1878, i, 104.

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if proper care and skill are used in carrying out the details of the work. I propose to point out those details which require special care in each method, and want of attention to which may cause serious errors in the results. The presence of titanic acid, unless the precautions mentioned in the method given in my report for the determination of P_2O_5 are observed, will be a fruitful source of error in either, and arsenic acid, unless carefully separated, will cause too high results, whichever method be used.

"1. In the molybdate method the first point to be observed is the destruction of the carbonaceous matter, especially in the case of irons and steel. I first observed this in 1877 in an investigation of Korschelt's method, which is mentioned in a paper by Hunt and Peters (*e*) to whom I communicated the fact in 1878. Finkener (*f*) mentioned the same thing in the same year, and says, very truly, '0.10 per cent. of P in a steel may easily be entirely overlooked by inattention to this fact.'

"2. If the solution of the steel or iron in HNO_3 is evaporated to dryness, and the residue is ignited to destroy carbonaceous matter, it must be redissolved in HCl, for very often the ignited ferric phosphate is quite insoluble in HNO_3. This requires repeated evaporations with HNO_3 to get rid of HCl, which is considered deleterious by such analysts as Fresenius and Finkener.

"3. Silica must be removed from the solution before adding the molybdate solution, unless the P_2O_5 be finally precipitated as $Mg_2(NH_4)_2P_2O_8$.

"4. After adding the molybdate solution, great care must be exercised on two points—the degree of acidity and the temperature of the solution. The phospho-molybdate of ammonia will not precipitate readily if the solution is too acid or the temperature too low, and a continued high temperature or boiling of the solution tends to the precipitation of an excess of molybdic acid with the ammonic phospho-molybdate. The most careful analysts direct that the solution should stand from 6 to 24 hours before filtering, and that the filtrate should

e Metallurgical Review, vol. ii, p. 365. *f* Deut. Chem. Ges. Ber., pp. 1638-1641.

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always be tested by a fresh addition of molybdate solution.

"5. If the P_2O_5 is finally weighed as $Mg_2P_2O_7$ it is very difficult to get rid of the last traces of molybdic acid. After two precipitations as $Mg_2(NH_4)_2P_2O_8$, I have found appreciable amounts of MoO_3 in the HCl solution of the ignited $Mg_2P_2O_7$.

"In the acetate method the first point which requires special attention is: 1. Driving off the excess of SO_2. It is very necessary to do this, as ferric phosphate is soluble in SO_2 and in ammonic sulphite.

"2. Both care and experience are necessary in neutralizing the deoxidized solution, for all the free HCl must be neutralized, and enough NH_4HO added to precipitate all the ferric phosphate and ferric oxide, and an excess over this should be avoided as tending to obscure the reaction and causing an excess of ammonic acetate, which is deleterious. On the other hand, if all the Fe_2O_3 is not precipitated, there will be loss, for ferric phosphate is soluble in ferric chloride.

"3. The precipitate of ferric phosphate and oxide should not be washed much (one washing is ample), as ferric phosphate is decomposed by pure water. My own personal preference is for the acetate method, and for the following reasons: 1. The sources of error are fewer and are more easily guarded against. 2. If the proper precautions are taken in each method, the acetate is the quicker. I have made many determinations (the accuracy of which was afterward proven by other results) in iron ores in 24 hours and in steels in 48. 3. There is not the same temptation in the acetate method that there is in the molybdate to take short cuts, which has brought many a young chemist to grief. 4. Experience has shown (*a*) that the molybdate method, as practiced by many chemists, is not as accurate although it may be shorter than the acetate.

"An accurate determination of P_2O_5, by whatever method it is made, requires much skill and not a little practice, and the advocate of one method often makes the other suffer, more by reason of his own want of skill in the manipulation of the

a E Riley, Jour. Chem. Soc., 1878, i, 104, besides numerous cases which have come under my own observation.

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other method than by reason of any great advantage inherent in his own.

Estimation of Silicon in Iron and Steel.—J. Jas. Morgan, Chem. News, **56**, 221. It is found that if the evaporation of the solution, obtained by treating four grms. of iron with aqua regia, be arrested upon its attaining a thick syrupy condition, so that it is with difficulty poured round the sides and bottom of the dish when given a circular movement, the silica obtained upon subsequent treatment with hydrochloric acid, is white and free from phosphorus and iron, as proved by fusion with acid potassium sulphate.

Determination of Titanic Acid,—Lucien Levy, Comptes rendus, October, 1887, 754. The author gives the results of experiments undertaken to determine the conditions under which a complete precipitation of pure titanic acid may be obtained by boiling. The following table shows the influence of varying amounts of free sulphuric acid :

No.	*Volume of the Solution*	*H_2SO_4*		*TiO_2*	
		Total.	*Free.*	*Contained.*	*Found.*
1.	100 c. c.	3.561 gr.	1. gr.	0.086 gr.	0.0829
2.	"	"	0.5	"	0.085
3.	"	"	0.00	"	0.100
4.	"	"	0.0	"	0.108
5.	150	5.766	5.766	0.036	0.000
6.	"	"	0.833	"	0.036
7.	"	"	0.000	"	0.047

The solution should be completely neutralized and then the requisite amount (about 0.5 per ct.) free H_2SO_4 should be added. Sulphate of zinc, magnesia, alumina and copper were found to have no influence on the purity of the precipitate. When sulphate of sesquioxide of iron is present the results are always too high.

Silica Determinations in Blast Furnace Cinder.—Clemens Jones, Trans. Am. Inst. Min. Eng., July, 1887. For procuring chilled samples of cinder for silica determination the author uses a cast-iron pan, similar to an assay pan, five inches

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square, and having in it four shallow, hemispherical cups. The pan has a handle 20 inches long, and the cups have the furnace-numbers countersunk in the bottoms. The sample is taken by filling this pan directly, or by means of a ladle, with the fluid cinder as it flows from the cinder notch. By this system there is no danger of confusion, and there are four small cakes from which to choose a final sample.

In cinders containing titanic acid, the silica obtained by the "acid method" was found to be contaminated with titanic acid. The author concludes that the acid method, when employed upon chilled cinders, and with proper precautions, is safe for all practical purposes. But chief among the precautions is a redetermination by the standard method in cases of marked variations in consecutive tests.

Want of Homogeneity of Basic Pig Iron.—C. R einhardt, Repertorium der analytischen Chemie, 1887, **49**, 742. Samples taken from different parts of pieces of basic pig iron often showed large differences in the phosphorus and manganese content, the outside of a piece almost without exception containing a considerably higher percentage of these elements than the interior. In an extreme case a sample from the outside contained 3.32 per cent. phosphorus, while the middle contained only 1.82 per cent. The manganese percentage increases and decreases with the phosphorus, but the variations are within narrower limits. The phosphorus and manganese were also found to vary in the different beds of a cast. The author advises that the sample for analysis be taken from the middle bed, and should contain an equal proportion of fragments taken from the outside and middle of the pig.

Sulphur and Graphite Determination in Iron.—Adolf Tamm, Jernkontorets Annaler, 1887. Stahl und Eisen, 1887, 627. For an accurate sulphur determination 5 grms. of iron are dissolved in a warmed mixture of 25 c. c. HNO_3, sp. gr. 1.40 and 25 c. c. HCl, sp. gr. 1.19. When solution is complete 0.1 gm. $KClO_3$ is added and evaprated to complete dryness. The dry mass is redissolved in 20 c. c. HCl sp. gr.

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1.19, diluted and filtered. 2 c. c. of a saturated solution of $BaCl_2$ is added to the filtrate and the whole is again evaporated to dryness. The residue is dissolved in 20 c. c. HCl sp. gr. 1.19 and diluted to 150 c. c. with boiling water. The $BaSO_4$ is filtered off, dried and ignited. It is fused with Na_2CO_3, the fused mass dissolved in hot water and filtered from undissolved $BaCO_3$. The filtrate is slightly acidified with HCl and precipitated with $BaCl_2$ solution. From the weight of pure $BaSO_4$ thus obtained must be taken the weight of $BaSO_4$ derived from the reagents used.

For a rapid colorimetric determination of sulphur the author uses Wiborgh's method (Chem. News, **54**, 158).

For the determination of graphite 2 grms. of pig iron are dissolved in at least 50 c. c. HNO_3 sp. gr. 1.20. The graphite, along with a little undissolved silica, is brought upon a weighed filter, dried at 100° C. and weighed. The filter and graphite are burned in a weighed platinum crucible and the residual silica is weighed. The weight of the silica is divided by 0.94, which gives the weight of the hydrated silica obtained by drying at 100° C. This weight, taken from the combined weight of graphite and silica, gives the weight of graphite.

ORGANIC ANALYSIS.

Valuation of Narcotic Extracts.—H. Beckurts Chem. Zeit. **11**, 1245. *Strychnine.*—2 gms. of the finely pulverized extract are dissolved in 5 c. c. water, 5 c. c. ammonium hydroxide and 10 c. c. alcohol. The solution is then extracted successively with 20, 10 and 10 c. c. chloroform. The chloroform extract is freed from chloroform by distillation. The residue is dissolved in 15 c. c. $\frac{1}{10}$ normal hydrochloric acid, heated on the water bath for several minutes, filtered from the separated resin, the filter washed and the filtrate and wash water titrated with $\frac{1}{100}$ normal caustic soda with cochineal as indicator. The number of c. c. of $\frac{1}{100}$ normal caustic soda used are subtracted from 150 and the remainder multiplied by 0.00364;

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this gives the quantity of alkaloid, which, multiplied by 50 gives the percentage amount, if we suppose strychnine and brucine to be present in equal quantities.

Hysocamus, *Belladonna*, *Aconite.*—2.5 gms. extract are dissolved in 3 c. c. alcohol, 6 c. c. water and 1 c. c. ammonia, and the solution extracted with 20, 10 and 10 c. c. chloroform. The extract is distilled, the residue dissolved in 5 c. c. $\frac{1}{10}$ normal hydrochloric acid, heated several minutes on the water bath, filtered from separated resin and the filtrate titrated with centinormal caustic soda and cochineal. The number of c. c. used subtracted from 50 gives the number of c. c. of $\frac{1}{100}$ normal hydrochloric acid required to neutralize the alkaloid.

$$1 \text{ c. c. } \frac{1}{100} \text{ normal HCl} = \begin{cases} 0.00289 \text{ Atropine.} \\ 0.00289 \text{ Hyoscamine.} \\ 0.00533 \text{ Aconitine.} \end{cases}$$

Conine cannot be estimated by this process on account of its volatility.

After titration the alkaloid should be extracted with caustic soda and chloroform and tested.

Estimation of Fusel Oil in Alcoholic Liquids.—J. Traube, Ber. **20**, 2644. Traube has modified the capillary apparatus figured on page 109, vol. 1, by flattering the end *c* of the lower tube into a flat disk with the perforation in the center, and has christened the apparatus "stalagmometer."

The wine or spirit to be examined is diluted with water so as to contain 20 volume per cent. alcohol and the number of drops from volume *V* is then counted and compared with that obtained from pure 20 per cent. alcohol at the same temperature. A plus number of about 1.6 in the first case corresponds to .01 per cent. fusel oil.

The test may be made more delicate by separating the fusel oil with ammonium sulphate as follows: 300 c. c. of the spirit diluted to about 20 per cent. is poured into a 400 c. c. stoppered separating funnel and about 110–120 gms. ammonium sulphate added. The mixture is now shaken for some time until the ammonium sulphate dissolves, causing the separation of the fusel oil and some of the alcohol which rise to

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the top. This upper layer is then separated carefully, diluted with water and distilled to one-third its bulk ; the distillate is then compared by means of the stalagmometer with 1st, a solution of pure alcohol of the same sp. gr., and 2d, with pure alcohol of the same sp. gr., containing measured amounts of fusel oil. This method gives three-fourths to five-sixths of the fusel oil contained in the alcohol ; a small additional amount may be obtained by adding a little alcohol and a few crystals of ammonium sulphate to the liquid left after the first separation and shaking again.

In making comparisons with the stalagmometer care must be taken that the lower disk is horizontal and that no vibrations are communicated to the apparatus.

The Stalagmometer: Its use as an Alcoholometer.—J. Traube, Ber. **20.** 2824. The method of using the apparatus is indicated in the preceding article. As the table given below runs as high as 10 per cent. of alcohol (by weight) only, when liquids contain a greater amount of alcohol they must first be diluted with water to reduce the amount contained below this figure. The pipette necessary for this purpose as well as the measuring flask is sold with the apparatus, which is supplied by C. Gerhardt, Bonn. Each apparatus has engraved upon it the number of drops *a* of water at 15° which it delivers and it is only necessary to multiply the number of drops found in any given case by $\frac{100}{a}$ and look for the number obtained in the table. In this table the number of drops of water delivered by the apparatus at 15° is taken as 100. The stalagmometer used for alcohol determinations is different from that used for the estimation of fusel oil, the tubes being of smaller bore. If the alcohol contains fusel oil it is of course necessary to apply a correction to the number obtained.

The stalagmometer may also (Ibid. 2829) be used for determining the alcohol in wine, beer, etc. In this case it is necessary to distill the liquid first with the addition of caustic potash to keep back the acetic acid. The ethereal oils have no influence upon the size of the drops. Neither has the small amount of glycerine which distils over any perceptible effect.

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Table for Determining the Amount of Alcohol from the Number of Drops.

Per cent. absolute alcohol by weight.	Per cent. absolute alcohol by volume.	Temperature in Centigrage Degrees.																				
		10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
0 00	0 00	92.2	99.4	99.5	99.7	99.8	100.0	100.2	100.3	100.4	100.6	100.7	100.9	101.1	101.2	101.4	101.5	101.7	101.9	102.0	102.2	102.4
0.20	0.25	101.0	101.2	101.3	101.5	101.6	101.8	102.0	102.1	102.3	102.4	102.6	102.8	102.9	103.1	103.3	103.4	103.6	103.8	103.9	104 1	104.3
0.40	0.50	102.5	102.7	102.9	103.0	103.2	103.4	103.6	103.7	103.9	104.0	104 2	104.4	104.5	104.7	104 9	105 1	105.3	105.5	105.6	105.8	106.0
0.60	0.75	104.0	104.2	104.4	104.5	104.7	104.9	105.1	105.2	105.4	105.5	105.7	105.9	106 0	106.2	106 4	106.6	106.8	107.0	107.1	107.3	107.5
0 80	1.00	105.4	105.6	105.7	105.9	106.1	106.3	106.5	106 6	106.8	106.9	107.1	107.3	107.4	107.6	107.9	108 0	108.2	108.4	108.6	108.8	109 0
1.00	1.25	106.8	107.0	107.2	107.3	107.5	107.7	107.9	108.0	108.2	108.3	108.5	108.7	108 8	109.0	109.2	109.4	109.6	109.8	110.0	110.2	110.4
1.20	1.50	108.2	108.4	108.6	108.7	108.9	109.1	109.3	109.4	109.6	109.7	109.9	110.1	110.2	110.4	110.6	110.8	111.0	111.2	111.4	111.6	111.8
1.40	1.75	109.5	109.7	109.9	110.0	110.2	110.4	110.7	110.8	111.0	111.1	111.3	111.5	111.6	111.8	112.0	112.2	112.4	112.6	112.8	113.0	113.2
1.60	2.00	110.8	111.0	111.1	111.3	111.5	111.7	111.9	112.1	112.3	112.4	112.6	112.8	113.0	113.2	113.4	113.6	113.8	114.0	114.2	114.4	114 6
1.80	2.25	112.0	112 2	112.3	112.5	112.7	112.9	113.1	113.3	113.5	113.7	113.9	114.1	114.3	114.5	114.7	114.9	115.1	115.4	115.6	115.8	116.0
2.00	2.50	113.1	113.3	113.5	113.7	113.9	114.1	114.3	114.5	114.7	114.9	115 1	115.3	115.5	115.7	115 9	116.1	116.3	116.6	116.8	117.0	117 2
2 20	2.75	114.2	114.4	114.7	114.9	115.1	115.3	115.5	115.7	115.9	116.1	116 3	116.5	116.7	116 9	117 1	117.3	117.5	117.8	118.0	118 2	118.4
2.40	3.00	115.3	115.5	115.8	116.0	116.2	116.4	116.6	116.8	117.0	117.2	117.4	117.6	117.8	118.1	118 3	118 5	118.7	119 0	119.2	109 4	109.6
2.60	3.25	116.4	116.6	116.9	117.1	117.3	117.5	117.7	117.9	118.1	118.3	118.5	118.7	118.9	119.2	119.4	119.7	119,9	120.1	120 4	120.6	120.8
2.80	3.50	117.5	117.7	118.0	118.2	118.4	118.6	118.8	119.0	119.2	119.4	119.6	119.8	120 0	120 3	120.5	120.8	121.0	121.2	121.5	121 7	121.9
3 00	3.75	118.6	118.8	119.1	119.3	119.5	119.7	119.9	120.1	120.3	120.5	120.7	120 9	121.1	121.4	121.6	121.9	122.1	122.3	122.6	122.8	123.0
3.20	4.00	119.5	119.7	120.0	120.3	120.5	120.8	121.0	121.2	121.4	121.6	121.8	122.0	122.2	122.5	122.7	123 0	123.2	123.4	123.7	123.9	124.2
3.40	4.25	120.4	120.6	120.9	121.2	121.5	121.8	122.0	122.3	122.5	122.7	122.9	123.1	123.3	123,6	123.8	124.1	124.3	124.5	124.8	125.0	125.3
3.60	4 50	121.3	121.5	121.8	122.1	122.4	122.7	122.9	123.2	123.4	123.7	123.9	124.1	124.3	124.6	124.8	125.1	125.4	125.6	125.8	126.1	126.4
3.80	4.75	122.2	122.4	122.7	123.0	123.3	123.6	123.8	124.1	124.3	124.6	124.8	125.1	125.3	125.6	125.8	126 1	126.4	126.6	126.8	127·1	127.4
4.00	5.00	123.1	123.3	123.6	123.9	124.2	124.5	124.7	125.0	125.2	125.5	125.7	126.0	126.2	126.5	126.7	127.0	127.3	127.8	127.6	128.1	128.4
4.20	5.25	124.0	124.2	124.5	124.8	125.1	125.4	125.6	125.9	126.1	126.4	126.6	126.9	127.1	127.4	127.7	128.0	128.3	128.6	128.8	129 1	129 4
4 40	5.50	124.9	125.1	125.4	125.7	126.0	126.3	126.5	126.8	127.0	127.3	127.5	127.8	128.0	128.3	128 6	128.9	129.2	129.5	129 8	130.1	130.4
4.60	5.75	125.8	126.0	126.3	126.6	126.8	127.1	127.4	127.7	127.9	128.2	128.4	128.7	128.9	129.2	129.5	129.8	130.1	130.4	130.7	131.0	131.3
4 80	5.99	126.7	126.9	127.2	127.4	127.6	127.9	128.2	128.5	128.8	129.1	129.3	129 6	129.8	130.1	130.4	130.7	131.0	131.3	131.6	131.9	132.2

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Table for Determining the Amount of Alcohol from the Number of Drops.

Per cent. absolute alcohol by weight.	Per cent. absolute alcohol by volume.	Temperature in Centigrage Degrees.																				
		10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
5.00	6.25	127.5	127.7	128.0	128.2	128.4	128.7	129.0	129.3	129.6	129.9	130.2	130.4	130.7	131.0	131.3	131.6	131.9	132.2	132.5	132.8	133.1
5.20	6.50	128.3	128.5	128.8	129.0	129.3	129.6	129.9	130.2	130.5	130.8	131.1	131.3	131.6	131.9	132.2	132.5	132.8	133.1	133.4	133.8	134.1
5.40	6.75	129.1	129.3	129.6	129.8	130.1	130.4	130.7	131.0	131.3	131.6	131.9	132.2	132.5	132.8	133.1	133.4	133.7	134.0	134.3	134.7	135.0
5.60	6.99	129.8	130.1	130.4	130.6	130.9	131.2	131.5	131.8	132.1	132.4	132.7	133.0	133.4	133.7	134.0	134.3	134.6	134.9	135.2	135.6	135.9
5.80	7.24	130.5	130.8	131.1	131.4	131.7	132.0	132.3	132.6	132.9	133.2	133.5	133.8	134.2	134.5	134.9	135.2	135.5	135.8	136.1	136.5	136.8
6.00	7.48	131.2	131.5	131.8	132.2	132.5	132.8	133.1	133.4	133.7	134.0	134.3	134.6	135.0	135.3	135.7	136.0	136.4	136.7	137.0	137.4	137.7
6.20	7.73	132.0	132.3	132.6	133.0	133.3	133.6	133.9	134.2	134.5	134.8	135.1	135.4	135.8	136.1	136.5	136.8	137.2	137.6	137.9	138.3	138.6
6.40	7.97	132.8	133.1	133.4	133.8	134.1	134.4	134.7	135.0	135.3	135.6	135.9	136.2	136.6	136.9	137.3	137.7	138.1	138.5	138.8	139.2	139.5
6.60	8.22	133.6	133.9	134.2	134.6	134.9	135.2	135.5	135.8	136.1	136.5	136.8	137.1	137.4	137.8	138.2	138.6	139.0	139.4	139.7	140.1	140.4
6.80	8.47	134.4	134.7	135.0	135.4	135.7	136.0	136.3	136.7	137.0	137.4	137.7	138.0	138.3	138.7	139.1	139.5	139.9	140.3	140.6	141.0	141.3
7.00	8.72	135.2	135.5	135.8	136.2	136.5	136.9	137.2	137.6	137.9	138.3	138.6	138.9	139.2	139.6	140.0	140.4	140.8	141.2	141.5	141.9	142.3
7.20	8.96	136.1	136.4	136.7	137.1	137.4	137.8	138.1	138.5	138.8	139.2	139.5	139.8	140.1	140.5	140.9	141.3	141.7	142.1	142.4	142.8	143.2
7.40	9.21	137.0	137.3	137.6	137.9	138.2	138.6	138.9	139.3	139.6	140.0	140.3	140.6	140.9	141.3	141.7	142.1	142.5	142.9	143.2	143.6	144.0
7.60	9.45	137.8	138.1	138.4	138.7	139.0	139.4	139.7	140.1	140.4	140.8	141.1	141.4	141.7	142.1	142.5	142.9	143.3	143.7	144.0	144.4	144.8
7.80	9.70	138.6	138.9	139.2	139.5	139.8	140.2	140.5	140.9	141.2	141.5	141.8	142.1	142.4	142.8	143.2	143.6	144.0	144.4	144.7	145.1	145.5
8.00	9.95	139.4	139.7	140.0	140.3	140.6	140.9	141.3	141.6	141.9	142.2	142.5	142.8	143.1	143.5	143.9	144.3	144.7	145.1	145.4	145.8	146.2
8.20	10.20	140.1	140.4	140.7	141.0	141.3	141.6	142.0	142.3	142.6	142.9	143.2	143.5	143.8	144.2	144.6	145.0	145.4	145.8	146.2	146.6	147.0
8.40	10.44	140.7	141.0	141.3	141.7	142.0	142.3	142.7	143.0	143.3	143.6	143.9	144.2	144.5	144.9	145.3	145.7	146.1	146.6	147.0	147.4	147.8
8.60	10.68	141.3	141.6	141.9	142.3	142.7	143.0	143.4	143.7	144.0	144.3	144.6	144.9	145.3	145.7	146.1	146.5	146.9	147.4	147.8	148.2	148.6
8.80	10.92	141.8	142.2	142.5	142.9	143.3	143.7	144.1	144.4	144.7	145.0	145.3	145.7	146.1	146.5	146.9	147.3	147.7	148.2	148.6	149.0	149.4
9.00	11.17	142.3	142.7	143.1	143.5	143.9	144.3	144.7	145.0	145.4	145.7	146.1	146.5	146.9	147.3	147.7	148.1	148.5	149.0	149.4	149.8	150.2
9.20	11.42	142.9	143.3	143.7	144.1	144.5	144.9	145.4	145.7	146.1	146.4	146.8	147.2	147.6	148.1	148.5	148.9	149.3	149.8	150.2	150.6	151.0
9.40	11.66	143.5	143.9	144.3	144.7	145.2	145.6	146.1	146.4	146.8	147.1	147.6	148.0	148.4	148.9	149.3	149.7	150.1	150.6	151.0	151.4	151.8
9.60	11.91	144.1	144.5	145.0	145.4	145.9	146.3	146.6	147.1	147.5	147.9	148.4	148.8	149.2	149.7	150.1	150.5	150.9	151.4	151.8	152.2	152.7
9.80	12.15	144.8	145.2	145.7	146.1	146.6	147.0	147.5	147.8	148.3	148.7	149.2	149.6	150.0	150.5	150.9	151.3	151.7	152.2	152.7	153.1	153.6
10.00	12.40	145.5	145.9	146.4	146.8	147.3	147.7	148.2	148.6	149.1	149.5	150.0	150.4	150.8	151.3	151.7	152.2	152.6	153.1	153.6	154.0	154.5

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The Stalagmometer: Its use as an Acetometer, as well as for determining the Alcohol in Vinegar, etc.—J. Traube, Ber. **20**, 2831 (see also the preceding articles). The instrument for alcohol may be used for this determination also. The method of conducting the operation is precisely as described above. The following table is intended for mixtures of water and pure acetic acid only. Where ethereal oils are present the results obtained are too high. Alcohol in acetic acid can be estimated, as in the case of beer, etc., by distilling with caustic potash and testing the distillate.

The author also points out some of the many determinations for which the stalagmometer may be used: as in mixtures of methyl alcohol and water, and in examination of urine.

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Table for Determining the Amount of Acetic Acid from the Number of Drops.

Per cent. pure acetic acid ($C_2H_4O_2$) by weight.	Temperature in Centigrade Degrees.									
	11	13	15	17	19	21	23	25	27	29
0.00	99.4	99.7	100.0	100.3	100.6	100.9	101.2	101.5	101.9	102.2
0.20	100.8	101.1	101.3	101.6	101.8	102.1	102.4	102.7	103.1	103.4
0.40	101.9	102.2	102.4	102.8	102.9	103.2	103.5	103.8	104.2	104.5
0.60	102.9	103.2	103.4	103.8	103.9	104.2	104.5	104.8	105.2	105.5
0.80	103.8	104.1	104.4	104.7	104.9	105.2	105.5	105.8	106.2	106.5
1.00	104.7	105.0	105.3	105.6	105.9	106.2	106.5	106.8	107.2	107.5
1.20	105.7	106.0	106.3	106.6	106.9	107.2	107.5	107.8	108.2	108.5
1.40	106.8	107.1	107.4	107.6	107.9	108.2	108.5	108.8	109.1	109.4
1.60	107.9	108.1	108.4	108.6	108.9	109.1	109.4	109.7	110.0	110.3
1.80	108.9	109.1	109.4	109.6	109.8	110.0	110.3	110.6	110.9	111.2
2.00	109.8	110.0	110.3	110.5	110.7	110.9	111.2	111.5	111.8	112.1
2.20	110.7	110.9	111.2	111.4	111.6	111.8	112.0	112.3	112.6	112.9
2.40	111.5	111.7	112.0	112.2	112.4	112.6	112.8	113.1	113.4	113.7
2.60	112.4	112.6	112.8	113.0	113.2	113.4	113.6	113.9	114.2	114.5
2.80	113.2	113.4	113.6	113.8	114.0	114.2	114.4	114.6	114.9	115.2
3.00	113.9	114.1	114.3	114.5	114.7	114.9	115.1	115.3	115.6	115.9
3.20	114.7	114.9	115.1	115.3	115.5	115.7	115.9	116.1	116.4	116.7
3.40	115.4	115.6	115.8	116.0	116.2	116.4	116.6	116.8	117.1	117.4
3.60	116.1	116.3	116.5	116.7	116.9	117.1	117.3	117.5	117.8	118.1
3.80	116.9	117.1	117.3	117.4	117.6	117.8	118.0	118.2	118.5	118.8
4.00	117.6	117.8	118.0	118.1	118.3	118.5	118.7	118.9	119.2	119.5
4.20	118.3	118.5	118.7	118.8	119.0	119.2	119.4	119.6	119.9	120.1
4.40	119.0	119.2	119.4	119.5	119.7	119.9	120.1	120.3	120.6	120.8
4.60	119.7	119.9	120.1	120.2	120.4	120.6	120.8	121.0	121.3	121.4
4.80	120.3	120.5	120.7	120.8	121.0	121.2	121.4	121.6	121.9	122.1

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Table for Determining the Amount of Acetic Acid from the Number of Drops.

Per cent. pure acetic acid ($C_2H_4O_2$) by weight.	Temperature in Centigrade Degrees.									
	11	13	15	17	19	21	23	25	27	29
5.00	120.9	121.1	121.3	121.4	121.6	121.8	122.0	122.2	122.5	122.7
5.20	121.5	121.7	122.0	122.1	122.3	122.5	122.7	122.9	123.2	123.4
5.40	122.1	122.3	122.6	122.7	122.9	123.1	123.3	123.5	123.8	124.0
5.60	122.7	122.9	123.2	123.3	123.5	123.7	123.9	124.2	124.5	124.7
5.80	123.3	123.5	123.8	123.9	124.1	124.3	124.5	124.8	125.1	125.3
6.00	123.9	124.1	124.4	124.5	124.7	124.9	125.1	125.4	125.7	125.9
6.20	124.5	124.7	125.0	125.1	125.3	125.5	125.7	126.0	126.3	126.5
6.40	125.1	125.3	125.6	125.7	125.9	126.1	126.3	126.6	126.9	127.1
6.60	125.7	125.9	126.2	126.3	126.5	126.7	126.9	127.2	127.5	127.7
6.80	126.3	126.5	126.8	126.9	127.1	127.3	127.5	127.8	128.1	128.2
7.00	126.9	127.1	127.4	127.5	127.7	127.9	128.1	128.4	128.7	128.8
7.20	127.5	127.7	128.0	128.1	128.3	128.5	128.7	129.0	129.3	129.4
7.40	128.1	128.3	128.6	128.7	128.9	129.1	129.3	129.6	129.9	130.0
7.60	128.7	128.9	129.2	129.3	129.5	129.7	129.9	130.2	130.5	130.6
7.80	129.3	129.5	129.8	129.9	130.1	130.3	130.5	130.8	131.1	131.2
8.00	129.8	130.0	130.3	130.4	130.6	130.8	131.0	131.3	131.6	131.7
8.20	130.4	130.6	130.9	131.0	131.2	131.4	131.6	131.9	132.2	132.3
8.40	130.9	131.1	131.4	131.6	131.8	132.0	132.2	132.5	132.8	132.9
8.60	131.4	131.6	131.9	132.1	132.3	132.5	132.7	133.0	133.3	133.4
8.80	131.9	132.1	132.4	132.6	132.8	133.0	133.2	133.5	133.8	133.9
9.00	132.4	132.6	132.9	133.1	133.3	133.5	133.7	134.0	134.3	134.4
9.20	132.9	133.1	133.4	133.6	133.8	134.0	134.2	134.5	134.8	134.9
9.40	133.4	133.6	133.9	134.1	134.3	134.5	134.7	135.0	135.3	135.4
9.60	133.9	134.1	134.4	134.6	134.8	135.0	135.2	135.5	135.8	135.9
9.80	134.4	134.6	134.9	135.1	135.3	135.5	135.7	136.0	136.3	136.4
10.00	134.8	135.0	135.3	135.5	135.7	135.9	136.2	136.5	136.8	136.9

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Note on the Elementary Analysis of Volatile Organic Compounds.—G. Kassner.* In the ordinary method of analysis it is not always possible to transfer the small vessel, containing a weighed quantity of the compound to be analyzed, into the interior of the combustion tube without loss of substance. It also frequently happens that after the analysis has begun there is a rapid volatilization of the substance, and a portion of it passes over unburnt into the calcium chloride tube.

The author endeavors to avoid these difficulties by taking a combustion tube somewhat longer than the furnace, and bends the end, that is to contain the substance, upward at an angle of about 30°. The small bulb containing the weighed substance may now be readily slipped into place without loss of material, by allowing it to glide down the inclined portion of the tube. As only the horizontal portion of the tube is heated, the volatilization takes place very gradually, and may be regulated without difficulty.

The Kopfer method of combustion, by means of platinized asbestos and oxygen, is recommended for volatile organic compounds because the combustion may be carried on at a lower temperature than is possible when the copper oxide method is used. It is also suggested that when halogen compounds are analyzed, the silver wire and foil commonly employed be replaced by silver asbestos. This may be prepared by mixing intimately finely divided silver obtained by reduction with short fibers of asbestos. X

On the Quantitative Determination of Sulphur and Halogens in Organic Compounds.—Peter Klason.† The combustion is effected by means of fuming nitric in an open combustion tube. The acid is introduced by means of rolls of platinum gauze containing glass beads. They are 5 cm. in length and 1 cm. in diameter, and each roll readily absorbs from 2–3 c. c. of the acid. The combustion tube is drawn out to a small diameter at one end, and the contracted portion is bent slightly, so that the products of combustion will readily

*Zeitschrift für analytische Chemie, **26**, 588.

† Ber. **20**, 3065.

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pass into a small receiver. In determinations of the halogens the receiver is partly filled with a solution of silver nitrate; in sulphur determinations the silver nitrate solution is replaced by distilled water.

The combustion tube is charged as follows: Into the end nearest the receiver are placed two rolls containing nitric acid, then two similar rolls free from acid are introduced, behind these is placed the boat with the substance; and finally two more nitric acid rolls immediately behind the boat complete the charge. The open end of the tube is connected with an air gasometer, and a slow current of air is allowed to pass through the apparatus. On heating the nitric acid rolls the air is charged with the oxides of nitrogen, and as soon as the substance is warmed the combustion begins. Care must be taken during the combustion to keep the front portion of the tube filled with brown fumes. After the tube has become cold, the platinum rolls and the interior of the tube are washed with water, and the wash water added to the liquid in the receiver. The sulphur is weighed as barium sulphate. The halogens are weighed as chloride, bromide or iodide of silver. X

TOXICOLOGY.

EDITED BY V. C. VAUGHAN.

Oxidation of Santonin.—After prolonged treatment with nitric acid, santonin furnishes acetic, succinic and hydrocyanic acids, with carbonic anhydride; with incomplete oxidation, oxalic acid is formed. Wagner in Berichte d. deutch. chem. Gesellschaft, B. 20, S. 1662.

Ptomains from Cultures of Vibrio Proteus—This bacterium in growing upon meat produces creatinine, methylguanidine and cadaverine. Bocklish in Berichte, B. 20, S. 1441.

Skatol from Strychnine.—Stoehr has also obtained skatol by distilling strychnine with lime. The skatol was recognized by its odor—that of faeces—and by an analysis of its picrate—ibid, S. 1108.

Color Reactions of Picric Acid and Dinitrocresol (Victoria

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Yellow).—When solutions of these substances are evaporated in a porcelain dish and the residue moistened with a little 10 per cent. hydrochloric acid, a small piece of pure zinc added, and the dish allowed to remain in the cold for some hours, a fine blue color is developed in the case of picric acid and a bright blood-red with dinitrocresol. In testing foods for these substances, an alcoholic extract of the food should be employed. Fleck in Chem. Centr. 1887, S. 99.

Andromedotoxin.— There is a toxical substance present in various species of the andromeda and first isolated by Pflugge: it can also be obtained from Rhododendron fonticum by infusion with water, concentration of the extract, precipitation of the albuminous substances with basic acetate of lead, and evaporation of the filtrate. It is best purified by frequent recrystallizations from chloroform and ether. Thus obtained, it forms in long needles, melts at 228°, is more soluble in cold, than in hot water; soluble in alcohol, its composition is $C_{31}H_{51}O_{10}$. In its chemical properties it is neither acidic nor basic, and it is not of the nature of a glucoside; it does not reduce silver salts, and gives no reaction with the heavy metals nor with alkaloidal reagents. Heated with dilute sulphuric acid, it gives a rose-red, and with hodrochloric acid a pale-yellow coloration. It is a powerful poison, diminishes the rate of respiration and produces paralysis. In these respects, it surpasses apomorphine. Zaaijer in *Rec. Trav. Chem.* T. 5, p. 313.

Toxic Action of Colchicine.—Colchicine acts as an irritant poison and attacks all the organs, but especially the digestive canal and kidneys. It is eliminated by the various secretions, but especially by the kidneys. However, the elimination is slow and it may behave as a cumulative poison. C.R. **104**, 439.

Origin of Ptomains.—It is possible that some of the basic substances found in putrefaction may be due solely to chemical agencies. The simple action of heating organic compounds with ammonia salts may give rise to basic products. The author has for a long time tried in vain to obtain poisonous bases from putrid meat by Maa's method. On treatment with

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anyl alcohol, a quantity of these bases was obtained from meat in various conditions of putrefaction, but they were all perfectly inert. The hydrochloric acid derivatives after heating on a water-bath were also inert, but the lactic acid compound, under similar treatment showed decidedly poisonous properties. This transformation of a non-poisonous into a poisonous product led to the study of the change of choline into the trimethylvinylammonium base. According to Brieger, the latter poisonous product is a frequent constituent of putrid matter, and arises from the action of putrefactive microphytes on choline. The same change can be effected by purely chemical means. The lactate of choline when heated gives rise to a poisonous substance with muscarine-like action. Inasmuch as many researches have shown that choline is widely distributed through animal and vegetable organisms, and as it is moreover capable of being converted into a poisonous substance by simple chemical action, it may be necessary to conduct researches on ptomains with more caution, and perhaps to regard with mistrust ptomains possessing a muscarine-like action. Gram in Chem. Centr. 1886, 647.

NEW BOOKS.

QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS—According to original methods by Dr. Alexander Classen, translated by Wm. Hale Herrick, A. M., 8vo. cloth, pages XI, 178, 47 illustrations, price $2.50. John Wiley & Sons. An electrolytic analysis, like an orchard, grows while you are sleeping, and electrolytic methods for this reason, if for no other, are bound to increase in favor. Prof. Herrick has done his work well. Some additions have been made when it seemed necessary, and have been made judiciously. The book is an English book—something which cannot be said of all translations—and deserves a place in the library of every chemist. It is well printed on good paper. E. H.

ORGANIC ANALYSIS: A manual of the descriptive and analytical chemistry of certain carbon compounds in common use. By Albert B. Prescott, Ph. D., M. D., pages VI, 533, 23 illustrations, price $5. D. Van Nostrand. This is really a dictionary of organic analysis and is one of the few indispensable

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books. Whether it entirely exhausts the subjects treated, can only be determined by using it. Prof. Prescott certainly deserves the thanks of the profession for this labor-saving volume. The book is nicely printed and illustrated and does credit to author and publisher. The limits of our space will, unfortunately, not admit of a fuller review of this excellent book.

E. H.

A LABORATORY GUIDE TO THE STUDY OF QUALITATIVE ANALYSIS by E. H. S. Binley, 44 pages, 8vo. For sale by Field & Hargis, Lawrence, Kansas. Alternate pages are left blank for convenience in taking notes. The plan of Fresenius is followed in the main, each metal being taken up separately; and each group of metals followed by the scheme of separation.

A TEXT-BOOK OF INORGANIC CHEMISTRY.—By Prof. V. vonRichter. Authorized translation by Prof. Edgar F. Smith. Third American from the fifth German edition. 12mo, 428 pages, $2.00. P. Blakiston, Son & Co., Phila. Prof. Richter's book is an excellent one; it cannot be said, however, that the translator has done his work well. This edition is a great improvement upon the first so far as the English of it is concerned, but it still limps in many places. Under nitrous acid in the first edition we read: "Its salts are obtained by glowing the nitrates". This is now rendered: "by igniting the nitrates." In the first edition under sulphuric acid: "It is now entered up on trade under the name crude sulphuric acid." This reads now, "upon trade under &c.," which is better but not best. Under molecular compounds, the first edition reads: "Especially demonstrating for the pentavalence of phosphorus is the, at ordinary temperatures, gaseous pentafluoride." This now reads "Phosphorus pentafluoride, a gas at ordinary temperatures, is a strong argument in favor of the pentavalence of phosphorus," which is much better. On the whole this edition is a great improvement upon the first. Prof. Smith is a good chemist but translation is certainly not his strong point. The mechanical execution of the book is good, except as to the illustrations, which are poor. E. H.

NOTES.

WHAT THEY EAT IN PARIS.*

Parisians are requested not to read this article, as we intend it only for our friends in the rural districts.

*Extract from "*l'Hygiene de la Famille*," Aug. 14, 1887.

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The story relates the wonderful adventures of four flies, who had made a long journey from the country for the purpose of feasting upon the delicacies of the capital of the civilized world. They had been told that edibles of the most delicious and varied kinds were exposed for sale in the streets of Paris, at the disposition of the flies. Accordingly they had come by a fast train, for, as we know, flies have the same freedom as the deputies on the railroads.

They followed the Rue de Rivoli. There was in the market place a marvellous selection of good things and the contents of the stalls appeared to the flies to much greater advantage than the heap of filth in which they were accustomed to obtain their nourishment at home. They held a consultation upon a lady's bonnet, near an artificial flower, the fresh glue of of which made it difficult for the flies to use their feet for walking purposes. They left the bonnet and resolved to separate and go into four shops which were near at hand.

The first fly presented herself at a butcher-shop, She *adored* sausage, to make use of a common expression.

The second fly preferred to test a sack of tempting flour of a very beautiful color.

The third entered the stall of a milk-woman. The milk there had such an abundance of cream that the fly had never seen any so beautiful before coming to Paris.

The fourth fly entered the shop of a grocer and druggist, but she saw there such a varied and novel collection of provisions that she hesitated which to try first.

Suddenly her companion at the butcher-shop fell from her beloved sausage and expired. The sausage was colored with aniline and the fly had been partaking of this violent poison.

The fourth fly, who still hesitated, now looked at her companion at the flour dealer's. As she did so, the second fly was seized with a burning sensation and fell over and died. She had been eating some of the plaster with which they adulterate flour at Paris.

The fourth fly, wishing to warn her remaining companion to beware of the dangers of Parisian progress, now directed herself to the milk-shop, when—heart-rending spectacle !—she saw the third fly struggle and die in the white liquid. The milk contained lime.

At this scene, the remaining fly, left alone and without hope in the great city of progress, resolved to put herself to death. Seeing a sheet of fly-paper at the druggist's, she threw herself

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upon it and drank furiously of the poison, in order to put an end to an insufferable existence.

But the more she drank the more she felt strengthened and comforted. She drank again, that she might join her companions in the kingdom of shadows. But she was cheered up and revivified and, far from producing death, the effect was delicious. Cruel fate ! the fly paper was not genuine !

This humorous sketch is from the facile pen of one of our fair readers, who has taken the idea from a Russian fable. The fable describes the misfortunes of the flies as having occurred in Germany, whilst our author places them at Paris.

I. A. P.

—The "*Repetorium der analytischen Chemie*" and the "*Zeitschrift fur die Chemische Industrie*" are to be consolidated under under the name of Zeitschrift für angewandte Chemie. The new journal is to be published upon the 1st and 15th of each month and will have the same general appearance as the Zeitschrift für die Chemische Industrie.

—According to Richardson, when a mixture of moist hydrochloric acid gas and moist oxygen is exposed to sunlight free chlorine is formed. See J. Chem. Soc. **51**, 801.

—On the occasion of the 101st anniversary of his birth, which occurred on the 31st of August last, the friends of M. Chevreul distributed a volume containing a list of all the memoirs, papers and notes published by him from the year 1806 to 1886, and which were collected by M. Godefroy Malloizet, assistant librarian in the Museum of Natural History at Paris. A superb portrait of the *savant* accompanies the volume. Two hundred and thirty-five pages are necessary to enumerate the titles only of the publications of M. Chevreul, while sixty-four pages are devoted to a list of the journals that have made extracts or published articles concerning the anniversary celebrations. Many of the addresses presented by different learned societies have been reproduced. The book is not sold but is distributed gratuitously to the subscribers to the medal struck in honor of M. Chevreul. M. Charles Brogniart was the leading spirit in the movement. I. A. P.

—Dr. Samuel Fenwick finds that the amount of potassium thiocyanate contained in the saliva of different individuals varies and that it varies in the same individual. He also finds that the amount of thiocyanate is below normal "whenever the digestive organs are unable to supply nutriment sufficient to meet the requirements of the system". The method used for making the determinations was colorimetric. *See Chem. News*, **56**, *259*.

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VOL. II. [APRIL, 1888.] PART 2

THE

Journal of Analytical Chemistry.

ON THE DETECTION OF COLORING MATTERS IN WHISKY.

BY J. H. LONG.

SOME three years ago in the course of an investigation on the character of a number of samples of whisky, placed in my hands by the internal revenue officers at Chicago, I found that the tests described in the books for the presence of caramel or other added coloring matter gave usually very unsatisfactory results. Nearly all samples examined gave distinct reactions with Fehling's solution, solution of barium hydrate and solution of lead acetate. When liquors are kept in barrels, whether charred or not, certain products of the nature of tannin are sooner or later taken up, and in order to obtain a reaction with the above reagents not due to these products, the latter were separated by digestion of the aqueous extract with cupric oxide. After filtration tests were again applied; in every case reduction of the Fehling solution or precipitation of the others was observed, although usually less marked than before treatment with the cupric oxide.

While these experiments were in progress an article by Amthor (Ztschr. anal. chem. **24**, 30) came to hand in which I found a suggestion of considerable value. Amthor had applied the paraldehyde reaction to the detection of caramel in this manner. To 10 c. c. of the liquid were added 30 to 50 c. c. of paraldehyde (according to depth of color) and enough absolute alcohol to cause the liquids to mix thoroughly. A brownish yellow precipitate found at the bottom of the vessel at the end

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of twenty-four hours consisted chiefly of caramel. The supernatant liquid was poured off and the residue was washed with absolute alcohol. It was then dissolved in a small amount of water and further tested by the ordinary methods, or best by the reaction with phenyl-hydrazine (suggested by Fischer, Ber. der deutschen chem. Gesch., XVII, 579). In applying this method to my samples I noticed great differences in their behavior, while some gave a heavy and characteristic precipitate with the paraldehyde, others gave only a trace, and still others no reaction whatever. Among the first and most interesting of the samples examined was one distilled in December 1884, and placed in my hands within a few days. It had the color and flavor of old whisky and was well calculated to deceive. 100 parts by weight contained .048 parts of solid residue obtained by evaporation on the water bath to complete dryness.

A strong reducing action was found with the Fehling solution, and with paraldehyde a heavy brownish precipitate was produced. This sample, as I learned by examination of a liquid seized with it, was colored with ordinary commercial caramel and flavored by a mixture of volatile oils and ethers.

The amount of dissolved solid matter appearing small I determined next how much was necessary to produce a color equal to that of average old whisky. For this purpose I dissolved various grades of liquid caramel, as sold in the market, in 50 per cent. alcohol to produce the shade of required depth. 50 gms. of these solutions evaporated to dryness gave residues weighing from .018 gm. to .050 gm., that is from .036 to .100 part per hundred. It requires, therefore, but a slight amount of burnt sugar color to produce the desired shade.

In the examination of six samples of genuine whisky, which had been distilled from two to four years before, I found that the solid residue amounted to .108 to .142 parts per 100. In an old sample distilled in 1865 and kept ten years in wood the residue amounted to .316 per 100. In six other pure samples which had been distilled less than six months before examinnation, I found amounts of residue varying between .028 and .069 per 100.

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All of these samples, the new as well as the old, gave slight reactions with the copper solution but gave nothing with paraldehyde, showing the value of the reagent.

I next turned my attention to whiskies which had been aged by a patent process in use in some parts of the country. In this process the whisky is placed in a tight barrel and heated by means of a steam coil introduced through the bunghole. The barrel is furnished with an upright condenser surrounded by a good water-jacket for the purpose of condensing the alcohol driven off by the continued heating. The action of the steam is sufficient in a few hours to cause the solution of notable amounts of coloring matter contained in the charred wood, and frequently the color developed is much deeper than could be developed by a natural ageing process. I examined fifteen samples superheated in this way and found the dissolved solids to range from .024 to .112 parts per 100.

In about half the samples in which the solids varied from .024 to .032 per 100 the color was comparatively light, while in most of the others in which the solids varied berween .040 and .112 parts per 100 the color was much darker than usually seen in any sample of naturally aged whisky. All these samples gave fair reactions with Fehling solution and likewise with paraldehyde. In those having the dark color the reaction with the latter reagent was very strong. This behavior led me to investigate the production of the coloring matter which is precipitated by paraldehyde. In describing the test Amthor cautioned against the concentration of samples by evaporation, as in this way, it appeared, a substance giving the paraldehyde reaction could be formed.

I had in my possession a large number of samples of pure whisky, naturally aged, and with them I made the following trials: Each sample was tested with barium hydrate, lead acetate and the copper solution, both before and after removal of tannin products. In every case some reaction was obtained; that is each liquid contained something which reduced Fehling solution and precipitated the other two. With paraldehyde nothing but a very slight light-colored precipitate could be obtained

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in any case. Then each sample was concentrated by evaporation to about one-third its volume and tested with alcohol and paraldehyde, as described above. In nearly every instance the characteristic brownish-yellow precipitate was thrown down within twenty-four hours. This showed clearly the effect of heat on the matter dissolved in the whisky. These substances were thereby converted into a product similar to or identical with caramel.

To obtain a better insight into this action I prepared mixtures of pure alcohol and distilled water having the strength of proof-spirit, and poured these mixtures over charred oak-wood cut in small pieces and preserved in glass stoppered bottles. The weight of the charred wood amounted to about half that of the diluted alcohol. In a few instances the proportions were somewhat different. In one series of experiments 250 gms. of well-charred wood was covered with 700 c. c. of diluted alcohol, and allowed to stand 22 days, with frequent shaking. At the end of this time 50 c. c. was withdrawn and evaporated to dryness giving a residue of .295 gm. At the end of 91 days the evaporation of another 50 c. c. gave .426 gm. In other experiments the solids taken up in six weeks varied from 69 to 885 parts per 100000 by weight. The mixture giving 69 parts was made from very deeply charred wood.

The solutions gave good reactions with lead acetate, barium hydrate and the Fehling liquid, but nothing characteristic of caramel with paraldehyde. I then transferred 50 c. c. of each solution to a flask holding 250 c. c. attached to an upright condenser, and boiled for five hours. In this way the artificial ageing process, mentioned above, was approximately duplicated. On now applying the paraldehyde test heavy precipitates were obtained, showing that an active conversion had taken place. The charring develops bodies closely related to caramel but it is only after the subsequent boiling that the identity is complete. This explains the behavior of the samples aged by the steam process, and the amount of caramel produced in this way was sufficient to show all the character-

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istic tests without giving any clew to its origin. It appears, therefore, that the proof of the actual addition of caramel to a liquor is an uncertain matter unless it is known that it has not been heated in contact with charred wood.

The proof of added flavoring matter is equally difficult and uncertain, as this can be supplied in many cases, in easily volatile form. When it is remembered that the total solids of a highly colored and highly flavored whisky need not exceed .100 part per 100, it will be seen that a conclusion drawn as to added flavor and color from a determination of solid residue may be quite erroneous.

CHICAGO, JANUARY 28, 1888.

COMPARISON OF METHODS OF TESTING INDIGO.*

BY HELEN COOLEY, S. B.

INDIGO analysis presents one of the most difficult problems of analytical chemistry. Out of the great number of methods of analysis proposed, those have been chosen for closer examination which have found acceptance among technical and analytical chemists. As experience has shown that methods which yield excellent results upon certain grades of indigo fail to give satisfaction when applied to other grades, it was thought best to test each method upon several grades. For this purpose ground samples of the following well-known varieties were prepared, viz.: Watson's Best, Bengal Blue, Kurpah Blue, Bengal Red, Oude, Guatemala, and Kurpah Red. As a standard, a quantity of indigotine was prepared by the action of sodium xanthate upon the commercial ortho-nitro-phenyl propiolic acid[1], purified by crystallization from aniline[2], and was finally sublimed. The analysis then gave the following result:

	Found. I	II.	Theory for $C_{16}H_{10}N_2O_2$
Nitrogen,	10.68	11.00	10.68

* From advance sheets of the *Technologist*; sent for publication by Prof. L. M. Norton.

1 Baeyer, Deutsches Reichs Patente, 11857, 11858, 14997.

2 Aguiar and Bayer Ann. Chem., 157, 366.

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SPECIFIC GRAVITY.

Leuchs[1] maintains that a relation exists between the per cent. of indigotine and the specific gravity of an indigo. In

	Indigotine by Fritsche's Method.	*Specific Gravity*
Kurpah Red	45.28	1.529
Guatemala	47.04	1.559
Oude	52.90	1.427
Bengal Red	54.03	1.391
Kurpah Blue	55.11	1.129
Bengal Blue	57.60	1.431
Watson's Best	59.53	1.292

general, the highest grade of indigo has the lowest specific gravity; but exceptions to this general rule are very numerous. Certain medium grades with a high per cent. of indigotine are very heavy; and where judgment is to be given concerning several samples of the same grade, this test is without value, as will be seen from the preceding table.

ESTIMATION OF THE ASH.

This estimation is commonly made in indigo testing, but is usually without the slightest value. In the following cases the ash was obtained by burning the indigo in a porcelain boat in a muffle.

	Indigotine.	*Ash.*
Kurpah Red	45.28	21.20
Guatemala	47.04	14.49
Oude	52.90	7.02
Bengal Red	54.03	6.41
Kurpah Blue	55.11	17.54
Bengal Blue	57.60	7.50
Watson's Best	59.53	6.50

DYEING TESTS.

On Cotton.—These tests were made with small vats, and in all cases zinc vats were used. Two grams of indigo were rubbed to a paste with water, and then washed into a large beaker. One gram of zinc dust and one gram of lime, in the

[1] J. prakt. Chem. N. F. 4, 349.

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form of milk of lime, was added, and the volume made up to 600 c. c. Pieces of cloth of equal weight were used for each sample, and the dyeing, squeezing, and exposure to the air, and also the temperature of the bath, were the same in all cases. The depth of color found was not in proportion to the amount of indigotine present in the various samples. The unreliability of the method is shown by the fact that, taking four samples of indigo, duplicate tests will almost always fail to show even the same gradation among the samples. It is, of course, true that no better method of testing indigo exists than the dyeing of large quantities of cotton, 5,000 pounds for example, with various samples, but satisfactory dyeing tests cannot be made upon swatches of cotton.

On Wool.—The conversion of the indigo into the disulphonic acid, by the action of strong sulphuric acid, and the coloring of wool with this acid, gives better results, although they leave much to be desired. Five tenths grams of indigo were digested with six grams of strong sulphuric acid in a warm place for twenty-four hours. The sulphonic acid thus formed was diluted to 1,000 c. c., and 10 c. c. taken for each swatch. The swatches weighed five grams, and were mordanted with five per cent. of sodium sulphate and three per cent. of sulphuric acid. They were then dyed under the same conditions, in every respect. The results give a rough idea of the value of the samples, but are not accurate enough to be of any considerable service.

LEE'S METHOD.

The idea of determining the per cent. of indigotine present in commercial indigo by removing it by sublimation and weighing the residue, is an old one. C. Tennant Lee[1] has given this method practical value by heating the indigo (0.2500 grams of dry indigo) in a platinum tray, upon which it can be very thinly spread. This tray is 7 cm. long, 2 cm. wide, and 1 mm. deep. The tray must be heated on an iron plate, and the temperature raised very gradually. A piece of Russia iron, bent in the form of an arch, is placed

[1] Chem. News, 50, 49.

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over the tray at a distance of 1 cm. Lee's instructions were followed with the utmost exactness.

	Indigotine by Fritsche's Method.	*Lee's Method.*
Kurpah Red	45.28	45.40
Guatemala	47.04	47.03
Oude	52.90	52.58
Bengal Red	54.03	55.99
Kurpah Blue	55.11	56.34
Bengal Blue	57.60	57.60–57.47
Watson's Best	59.53	59.42
Indigotine	99.71	95.75–94.02

These results show that, in general, Lee's method gives very satisfactory results. There may be an error from the carbonization of indigotine giving too low results, and also from the decomposition of the organic matter present giving too high results. The method is rapid, never requiring more than one hour.

FRITSCHE'S METHOD.

Fritsche[1] reduces the indigotine to indigo white, and then precipitates and weighs the indigotine in an aliquot part of the solution of indigo white. This method of analysis was executed in the following manner: Flasks were graduated containing 525 c. c., and fitted with rubber stoppers with two perforations; a short, bent tube passed through one hole, and a tube reaching nearly to the bottom of the flask through the other. These were fitted with rubber tubes and clamps. One gram of very finely powdered indigo was placed in the flask, 20 c. c. of potassium hydrate solution containing 40 per cent. of KOH, and five grams of grape sugar dissolved in a little water, were added, and the flask was filled nearly to the mark with alcohol. The stopper was then inserted, the long tube was raised nearly to the cork, and the tubes left open. The flask was warmed gently for thirty minutes on a water-bath. The tubes were then closed, and the flask allowed to stand over night. In the morning the flask, which now contained

1 Ann. Chem., **44**, 290.

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an alcoholic solution of indigo white, was gently heated until the liquid reached the graduation. The long tube was now lowered, the short tube attached to a hydrogen generator, and portions of 100 c. c. forced out. The portion of 100 c. c. was transferred to a beaker and a blast of air blown through, and by this the indigotine was precipitated in a crystalline form. The indigotine was filtered upon a weighed filter previously prepared by passing a similar solution of potassium hydrate and glucose in alcohol through it, dried at 110°, and weighed. This method is not accurate in inexperienced hands, but gives good results after practice. The results obtained by this method, after practice upon a single variety, are as follows:

	Per cent. of Indigotine.	
Oude	52.86	52.78
Bengal Red	53.54	54.03
Bengal Blue	56.46	57.65
Kurpah Blue	55.11	55.32
Kurpah Red	45.28	
Guatemala	47.04	47.16
Watson's	59.51	59.59
Indigotine	98.50	99.71

These results check much better than those that were obtained by any other method, and are undoubtedly very close to the truth.

NORTON'S METHOD.

This method was first described, in the form used, by L. M. Norton, in 1880[1]. By this method the indigotine is reduced to indigo white, and the solution of indigo white added to a ferric solution. The amount of ferrous salt formed by the reducing action of the indigo white is then determined by titration with an oxidizing agent. One gram of finely powdered indigo was placed in an agate mortar, and rubbed with milk of lime. The paste was washed into a flask prepared as for Fritsche's method, one gram of zinc dust added, and the flask filled to the mark with water. It was heated for thirty minutes on a water-bath, closed, and allowed to stand over

[1] Proc. Amer. Asso. Adv. Science, 1880, 358.

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night. It was thoroughly shaken in the morning, allowed to settle, and portions of 100 c. c. forced off by hydrogen as in Fritsche's method, and poured into an iron alum solution. The ferrous salt formed was then titrated with potassium bichromate solution. The manipulation is much less difficult than with Fritsche's method, and the time required is less. Some practice is necessary to obtain good results.

	Fritsche's Method.	*Norton's Method.*
Kurpah Red	45.28	45.40
Guatemala	47.04–47.16	47.03
Oude	52.86–52.78	52.58
Bengal Red	53.54–54.03	55.99
Kurpah Blue	55.11–55.32	53.34
Bengal Blue	56.46–57.65	57.47–57.6
Watson's Best	59.51–59.59	59.42
Indigotine	98.50–99.71	94.02–95.75

The method gives satisfactory results.

M'KINLEY'S METHOD.

The oxidation methods all depend upon the destruction of sulphindigotic acid by a known quantity of an oxidizing agent, and the consequent disappearance of a blue color in the solution thus treated. McKinley[1] dissolves three tenths of a gram of indigotine in eight parts by weight of fuming sulphuric acid by heating, at 55° C., in a small glass-stoppered bottle, for from eight to ten hours. The solution is then washed into a porcelain dish, diluted to 500 c. c., and an oxalic acid solution containing five times the weight of the indigo added. It is then warmed, and titrated with bichromate of potash solution of about five grams to the liter. The blue color passes through green to an olive, and the end point is easily recognized with pure indigotine. The pure indigotine was used for standardizing the bichromate, and the samples dissolved and titrated in exactly the manner described above. The end point was more difficult to recognize. Certain samples can be tested by this method, but in general the results are unreliable, as the following table shows:

[1] Chemical News, 8, 284.

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	McKinley's Method.	*Fritsche's Method.*
Oude	52.42–52.58	52.86
Bengal Red	62.16	53.54–54.03
Bengal Blue	65.54–63.10	56.4 –57.6
Kurpah Blue	66.72–57.86	55.11–55.32
Guatemala	62.56	47.12–47.04

ULLGREN'S METHOD.

Ullgren[1] makes his solution exactly as McKinley recommends. This indigo solution is made up to one liter, one hundred cubic cent. taken, placed in a porcelain dish, freely diluted, sodium carbonate added in excess, and this solution titrated with potassium ferricyanide solution containing three grams to the liter. Pure indigotine was used for standardization, and the indigo samples treated similarly. With a rapid titration the results are from fifteen to twenty per cent. too high. By regulating the time allowed for each addition of ferricyanide to take effect, the skillful operator can obtain any desired result. The Oude indigo gave from 54.5 to 80.0 per cent. of indigo blue.

RAWSON'S METHOD.

Rawson introduced his method[2] to meet the difficulties caused by the oxidation of organic matter other than indigotine. One gram of ground indigo was mixed with powdered glass in an agate mortar, and added gradually to 20 c. c. of concentrated sulphuric acid in a large porcelain crucible.

The crucible was allowed to stand for two hours at 90° C.; the solution was then made up to one liter, and filtered. Thirty grams of sodium chloride were added to 50 c. c. of the filtrate. This causes a precipitation of the sulphindigotic acid as the sodium salt. This was filtered off and washed with 50 c. c. of concentrated salt solution, and then dissolved on the filter in hot water, cooled, 1 c. c. of sulphuric acid added, and the solution titrated with potassium permanganate solution. The permanganate was standardized with pure indigotine. Rawson makes an allowance of .0008 gm. of indi-

1 J. Chem. Soc., 1865, 217.
2 Chemical News, 51, 255. Dyer and Calico Printer, April, 1887.

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gotine for the amount remaining dissolved in the salt solution. This is sufficient in the case of indigotine, but certain indigos were found from whose solution salt refused to precipitate the sulphindigotic acid with any completeness. In spite of this fact the method gives generally too high results, and the precipitation of the sodium salt cannot be accomplished without bringing down other organic matter.

	Rawson's Method.	*Fritsche's Method.*
Bengal Red	64.10	53.54–54.03
Bengal Blue	60.89	56.46–57.65
Oude	51.87–51.9	52.86–52.78

SPECTROPHOTOMETRIC METHOD.

This method, described by C. H. Wolff[1] and others[2], was examined, and the instrument used exactly as is described. The indigo (0.5 gm.) was dissolved in 5.0 gm. of sulphuric acid of 66° B., by allowing it to stand in a warm place for twenty-

	Spectrophotometer.	*Fritsche's Method.*
Kurpah Red	25.8–30.20	45.28
Guatemala	28-3–40.1	47.04–47.16
Oude	22.2–28.3	52.86–52.78
Bengal Red	39.6–51.1	53.54–54.03
Kurpah Blue	51.5–55.6	55.11–55.32
Bengal Blue	56.9–57.55	56.46–57.65
Watson's Best	58.5–58.8	59.51–59.59

four hours. The solution was then diluted to 1 liter, and 25 c. c. taken and again diluted to 1 liter, and this solution examined in the spectrophotometer. The results were far too low, and indicated an incomplete decomposition of the indigo. Stronger acid, finally equal parts of strong sulphuric acid and Nordhausen acid, were used, but without any marked improvement. The method gives fair results upon high grades, but low-grade indigos cannot be examined by this method.

SUMMARY.

In order to compare the results obtained by the different methods on the same sample, and to show the working of the

[1] Ztschr. anal. Chem., 1878, 65. [2] Vierordt and Hufner.

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methods, the following table is presented. It shows the average per cent. obtained by the different methods, as given above.

METHODS.

	Sp. Gr.	*Ash.*	*Lee.*	*Fritsche.*	*Norton.*	*McKinley.*	*Ullgren.*	*Rawson.*	*Spectrophotometer.*
Kurpah Red	1.529	21.20	45.40	45.28	45.48				25.-30.
Guatemala	1.559	14.49	47.03	47.10	47.14	62.56			28.-40.
Oude	1.427	7.02	52.58	52.72	51.53	52.50	54.-80.	51.88	22.-28.
Bengal Red	1.391	6.41	55.99	53.79	53.13	62.16		64.10	39.-51.
Kurpah Blue	1.129	17.54	56.34	55.21	55.23	62.			51.-55.
Bengal Blue	1.431	7.50	57.54	57.06	57.27	64.27		60.89	57.23
Watson's Best	1.292	6.50	59.42	59.55	59.32				58.65
Indigotine			94.88	99.10	98.44				

It is evident from this table that certain samples of indigo offer much greater analytical difficulties than others. It is not improbable that the claim of merit for certain analytical processes may have come from tests made upon a single sample of indigo. If McKinley's and Rawson's methods were to be judged by the results obtained in the analysis of the Oude indigo, they would be pronounced excellent methods. The preference is to be given to the methods of Fritsche, Norton, and of Lee. Either is reliable in practiced hands. The failure of the oxidation methods is due to the fact that the oxidizing agents act not only upon the indigotine, but upon other organic matter. An easy and reliable method, which can be employed for indigo analysis by the general analyst, is much to be desired.

Mass. Institute of Technology.

RAPID FILTERING APPARATUS.

By Geo. C. Stone.

Figures 1, 2 and 3 show a filtering arrangement which I have used for some time and which has worked very satisfactorily. A long glass tube with six branches rests on the upper bar of the stand, the straight end is connected with the pump by a rubber tube; each branch is connected with a flask by a piece of rubber tubing about six inches long and a bent glass

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tube which just passes through one hole in the cork, the funnel being placed in the other. It has the advantage over the arrangement described by Mr. Jones,* that any flask can be removed without interrupting the use of the rest by closing the rubber tube with a screw clamp.

Figure 8 is an improved form of screw clamp which I had made to overcome the faults of the ordinary style. I found that as usually made the clamps were much too light and made of too soft brass so that the thread of the screw stripped, the upper bar bent and the side pieces pulled through the ends, and also that the end of the screw soon ground a hole in the rubber tube that it was used to close. The clamp shown is made of hard brass and heavy with large rivet heads to the side bars and has a plain bar between the end of the screw and the tube.

While this arrangement worked very well for general purposes we found that the rubber connections were rapidly attacked by nitric fumes, and as we used it principally for volumetric determinations of manganese in spiegel† we finally adopted the arrangement shown in figs. 5, 6 and 7. The apparatus consists of a tube three-fourths of an inch in diameter, with branch tubes about seven-sixteenths of an inch in external diameter. The tube is supported by a wooden stand so that six of the branch tubes point upwards, the seventh points down and is connected to a flask by a rubber stopper. At the back of the stand is a narrow shelf with pegs for draining the funnels. One end of the main tube is bent up at a right angle for convenience in washing, and is closed by a rubber stopper when the apparatus is in use. Short pieces of rubber tube are slipped over the open ends of the branch tubes and the stem of the funnels. When a funnel is removed the opening is closed by a pointed glass plug of the same diameter as the stem of the funnel. For our especial object there is no advantage in saving the filtrates separately, so that we have but one

*Jour. Anal. Chem., Vol. I, p. 383.

†The method used is to dissolve in HNO_3 sp. gr. 1.43, precipitate by $KClO_3$, filter, reduce by standard $H_2C_2O_4$ and titer the excess with $K_2Mn_2O_8$.

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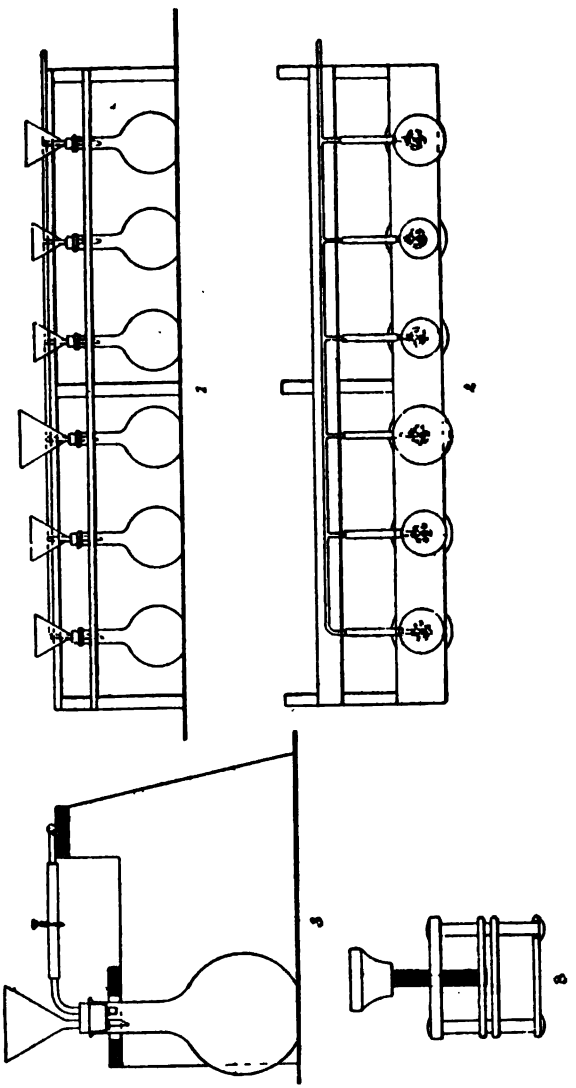
flask connected with the tube. By having a downward branch under each upward one the filtrates could be saved separately. I use two such tubes connected at their lower ends by a three-way cock which permits either or both to be connected with the pump.



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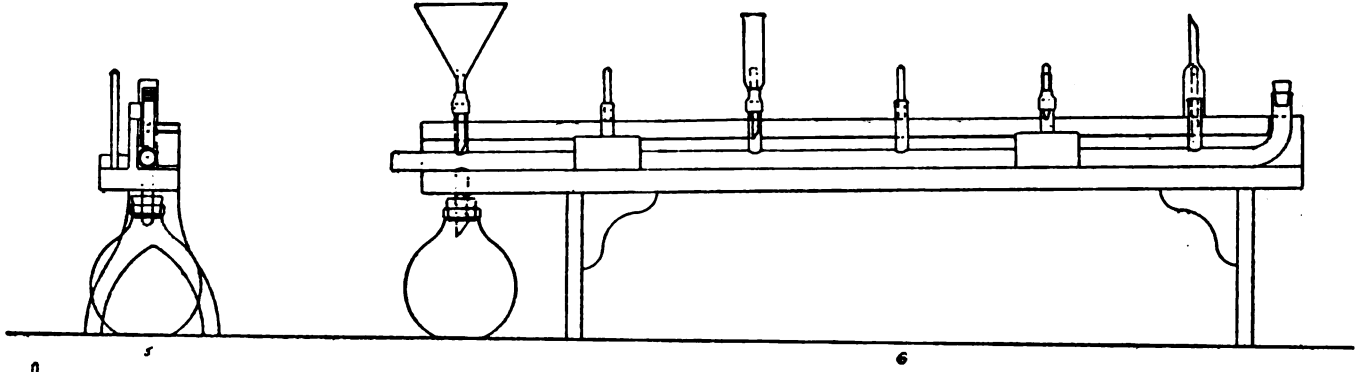

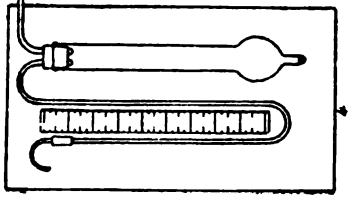

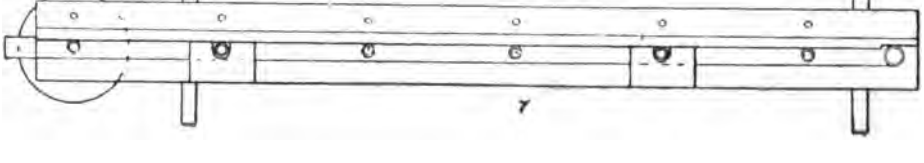

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Figure 4 is a gauge and guard tube which we have attached to the pump. It consists of a large $CaCl_2$ tube with the small end bent at a right angle and connected with the pump by a rubber tube, in case the pump "floods" the water is caught in this tube and does not get back to the analysis. The upper end of the guard tube is closed by a rubber stopper with two holes, one of which is connected by suitable tubing with the apparatus to be exhausted, the other with a mercury gauge which shows immediately any leak in the connections. These last two arrangements were gotten up by my former assistant Mr. W. W. Burritt.

DETERMINATION OF SILICA IN BLAST FURNACE CINDER.

By R. H. Lee, Jr.

In view of the discussion over the relative values of the two methods for determining silica in cinders, the fusion and the hydrochloric, I offer the method I have been using for the last four years with excellent results both as to accuracy and quickness.

Some four years ago the principal ore used in the furnace changed its character from a brown hematite to a hard carbonate, carrying irregularly from two to four per cent. of sulphur in form of pyrites. Kilns were put up which reduced the sulphur about half, but still left an inconveniently large amount in the stock, and at this time the composition of the cinder became of importance, as a cinder without sufficient lime invariably resulted in white iron and an excess of lime consumed extra coke. Under these circumstances I had to make a great many cinder analyses, and not having very much uninterrupted time to devote to the laboratory, it was necessary to find some method of decomposing cinder more rapid than the old method of fusion with Na_2CO_3 or the mixed carbonates. My first attempts were naturally with HCl and with not very

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good results, much of the cinder remaining untouched, covered with a coating of gelatinous silica. However on working the method up I found that the entire trouble was due to one cause only—not sufficient care being taken to keep the pulverized mass broken up and all portions exposed to the action of the acid. Neglect of this always gave high results, while if attention was paid to this point the results agreed well with those obtained by fusion, whether the cinder had previously been chilled or not, the only difference being that in the former case the decomposition seemed a trifle more rapid. The working details are as follows :

Take one-half gram finely powdered cinder and brush over the bottom of a large beaker, capable of holding about a liter when full. Over the cinder pour from one-half to five-eighths inch of *concentrated* HCl. The cinder on the bottom will form in patches and stick there ; these must be broken up by scrubbing with a glass rod covered with a rubber. Put on the hot plate and cover with a watch glass and heat a few minutes. Take off and repeat the scrubbing operation, breaking up any little flocks and masses that may be seen and loosen any material sticking to the bottom. This will have to be repeated at intervals of every few minutes until all the cinder is decomposed, which is easily told by the disappearance of grains and by the silica becoming gelatinous. The scrubber may be rinsed into the beaker each time by a few drops of water, but the less water used the better. When the cinder is decomposed, remove the watch glass and evaporate until all free acid seems driven off, then add about one-eighth inch more concentrated HCl and run down to dryness and until all fumes are driven off. This second addition of acid is not perhaps necessary but only done as a precaution. I keep the plate as hot as possible during the evaporation without risking spattering.

The dry mass is moistened with concentrated HCl, put on the plate and heated until all traces of iron are dissolved, water added, heated and filtered and the silica thoroughly washed with hot water. The results, if sufficient care has been taken to

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break up any flocks and masses, will agree with the fusion method. The time required is from two to two and a half hours. I have used this method with both coke and charcoal cinder.

I append a few duplicates made recently, mostly by Mr. W. A. Stevenson of Lehigh University. Want of time preventing me from making a greater number, they will show, however, about how the two methods run in ordinary work. A half gram being taken in each case, a lesser amount in my judgment being liable to introduce greater liability of error from slight inequalities in weighing or the losses during manipulation.

Cinder.	*HCl.*	*Fusion.*
No. 1	35.35	35.42
" 2	36.46	36.44
" 3	35.70	35.78
" 4	37.86	37.94
" 5	37.98	37.76
" 6	32.54	32.61

NOTE BY THE EDITOR.—This paper will also be read at the Boston meeting of the American Institute of Mining Engineers. In a letter accompanying the MS., Mr. Lee says: "There is one feature in decomposing cinders by HCl not alluded to in the paper, since I do not know the cause and have had no time to investigate, and that is, some cinders, although treated exactly alike refuse to decompose readily, and in spite of scrubbing and breaking up keep in granular form, requiring sometimes an hour or two to finally resolve. In such cases, to save time, I generally throw the analysis away, and weighing out another half gram, of the same cinder and same pulverized sample, decompose it without difficulty. Why the same cinder should act so differently I do not know but think it must be due to some action of the acid when first poured on the cinder."

Since the foregoing was printed the following letter has been received from Mr. Lee:

LEWISTOWN, PA., March 13, 1888.

"PROF. EDWARD HART: *Dear Sir*—Your note and enclosed cinders of 6th received and analyzed for silica. The pieces chilled in water I found gave 47.02 and 47.14 per cent. SiO_2 by HCl, but the one allowed to cool slowly I was unable to decompose by HCl, although I dropped the pulverized cinder into the acid in small portions and boiled for over six hours. Two samples, which I had boiled in acid for about thirty minutes, seemed so slightly attacked that I went on farther with them. The third after the six hours gave 61.16 per cent. SiO_2. I made no fusion determinations owing to my blast lamp being away for repairs and a Bunsen burner with gasoline gives a heat not much above the melting point of Na_2CO_3. I find I will have to modify my views as to all cinders being easily decomposed by acid, and would rather withhold my paper until I, or some one else, can write the subject up a little more completely.

Yours very sincerely, R. H. LEE, JR."

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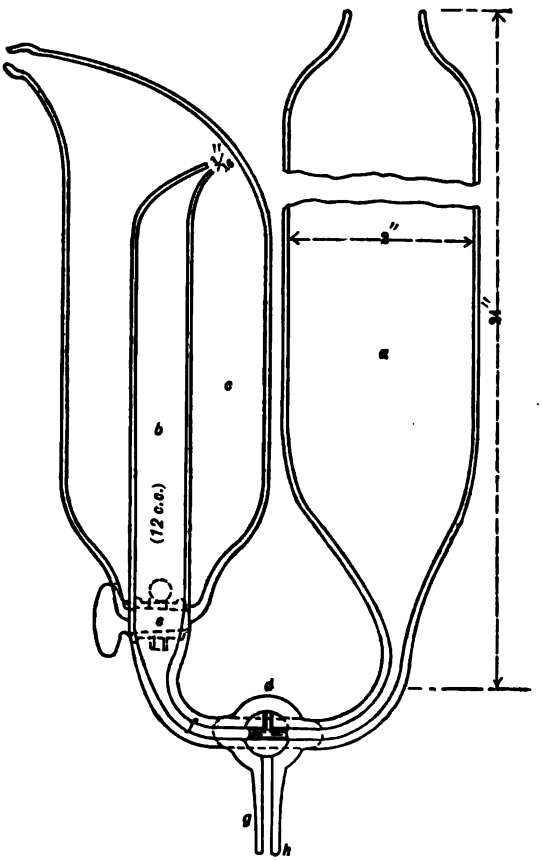
MEASURING APPARATUS.

By G. P. Vanier.

It often happens that one wishes to measure accurately and rapidly equal successive portions of a liquid. With the above object in view the following apparatus was devised. It is used for measuring out equal portions of HNO_3, in dissolving steels in Eggert's color method for carbon. The liquid to be measured is placed in (a). To measure out a portion of the liquid, the three-way-cock (d) is turned to allow the pipette (b) to fill and overflow into (c). As soon as the pipette begins to overflow the cock is turned and the pipette allowed to empty itself. The overflow liquid, which collects in (c), after a number of measurements is run out through stopcock (e) and returned to (a). The bore of the lower part of the pipette and of the drain from the cock (d) should be about ⅛ inch in diameter. As soon as the stream breaks at (h), in emptying the pipette, the measurement is complete, it not being necessary to allow any time for the pipette to drain. The liquid that drains down the sides is held by capil-



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lary attraction at (f); and the drop that hangs at (h) when the stream breaks is drawn back into the end of (g). The sum of 50 measurements of 12 c. c. each, made in 4 minutes, differed less than $\frac{4}{10}$ of a c. c. from the sum of 50 other measurements made in the same time, which means measuring 12 c. c. to within $\frac{1}{125}$ of a c. c. in less than 5 seconds.

THE ESTIMATION OF SUGAR, STARCH AND ASH-CONSTITUENTS IN FODDER.*

By E. F. Ladd.

The determination of sugars and starch in feeding stuffs has been made as follows:

Sugars.

Five grams of substance are brought upon a filter and washed with water until the filtrate amounts to 200 c. c. Ten cubic centimeters (0.25 gram substance) of this solution are taken, and the sugar determined by Fehling's solution. This gives the invert sugar, glucose, etc., or water soluble extractive matter capable of reducing copper.

Another portion of the filtrate is heated on the water-bath for one-half hour with a few drops of HCl, then neutralized with sodium carbonate, and the sugar determined by Fehling's solution, as in the previous case. The difference between the two determinations gives the amount from sucrose, or water soluble matter inverted by HCl.

Starch.

Five grams of the substance are put in a flask of 250 c. c. capacity, 150 c. c. of distilled water and four to five c. c. of concentrated HCl added, and the flask closed by a cork carrying a small glass tube about three and one-half feet in length, which acts as a condenser. The flask is then put in a water-bath kept at 100° C, for twelve hours, which time seems to be sufficient to invert the starch. The flask is allowed to stand over night; the solution is then filtered off, the

* From Report of the New York Agricultural Experiment Station, 1887, p. 462.

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filtrate made alkaline by sodium carbonate, and the washing continued until the filtrate amounts to 200 c. c. The sugar is then determined in 10 c. c. of the filtrate, by Fehling's solution, and the starch calculated from the sugar, or better, by reading directly from a plotted chart the amount of starch for the permanganate solution required.

The ash from a considerable number of feeding stuffs has been more or less fully analyzed, especially as regards the fertilizing constituents, and the method pursued was as follows:

Ash Analyses.

The substance for ash analysis is burned in the same manner as for ash determination in fodder analysis, at low heat, then thoroughly pulverized in an agate mortar and preserved in well-stoppered bottles until wanted for analysis.

Solutions.

One gram of ash is weighed into a platinum evaporator, and a little water added, then a small glass funnel is inverted in the evaporator and HCl cautiously added until effervescence ceases, then a few drops of HCl, in excess, and the whole evaporated to dryness. The residue is then moistened with HCl, and water added and heated on water-bath for a few minutes, then filtered through a tared Gooch crucible. The residue is sand, silica and carbon, dried, weighed, ignited, loss taken as carbon, remainder as sand and silica.

The filtrate is made up to 200 c. c., and 50 c. c. used in each of the following: A, B and C:

A. Sulphuric Acid.

Fifty cubic centimeters of the filtrate are made up to 100 c. c., or more, heated to boiling, and barium chloride added and then filtered; precipitate is barium sulphate.

Alkalies.

The filtrate from the above is heated and barium hydrate added in excess, then filtered, washed, to filtrate 1 c. c. ammonia is added, then ammonia carbonate, and heated, then about 0.5 grams oxalic acid added and filtered, washed thoroughly

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with hot water, filtrate evaporated to dryness, ignited gently to drive off ammonium salts, then dissolved in water and a few drops of HCl added, and filtered into a tared evaporator and again brought to dryness, ignited gently at low heat, cooled and weighed as total alkalies.

POTASH.

The above residue is dissolved with water in a porcelain evaporator and platinum chloride added, evaporated on steam-bath nearly to dryness, but not enough to drive off the water of crystallization, alcohol (80 per cent.) added, and allowed to stand for fifteen minutes, alcohol then decanted and precipitate repeatedly washed with alcohol, then the precipitate is brought upon a tared Gooch crucible, washed with a little ether and dried at 100 C. for thirty minutes and weighed.

SODA.

Soda is determined by difference between potash and total alkalies.

B. IRON AND ALUMINA.

Fifty cubic centimeters of the original solution were made alkaline with ammonia then acetic acid added in excess. The precipitate may be ferric and aluminic phosphate, but is weighed as $Fe_2(PO_4)_2$.

LIME.

The filtrate from the last is heated and ammonium oxalate added, then allowed to stand in a warm place for a few hours and filtered, washed, dried, ignited intensely and weighed directly as CaO.

MAGNESIA.

The last filtrate is made alkaline with ammonia, and then sodium phosphate added and allowed to stand, then filtered, washed, dried, ignited and weighed as $Mg_2P_2O_7$.

C. PHOSPHORIC ACID.

Fifty cubic centimeters of the original solution are taken, heated, and about 15 grams of ammonium nitrate added, then for every decigram of P_2O_5 50 c. c. of molybdic solution are

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added, kept for one hour at about 65 C., then a few c. c. of the clear solution are tested in a test-tube by adding fresh molybdic solution and heating over a flame; if a precipitate forms, it is filtered and washed with ammonium nitrate solution. The precipitate is dissolved on the filter with ammonia and hot water, filtrate nearly neutralized with HCl, allowed to cool, then magnesia mixture slowly added, stirring constantly. After 15 minutes 25 c. c. ammonia are added and allowed to stand two hours or more, then filtered through a tared Gooch crucible, washed with dilute ammonia, dried, ignited intensely and weighed as $Mg_2P_2O_7$.

IRREGULAR DISTRIBUTION OF SILICON IN PIG IRON.

By John W. Thomas.

In analyzing samples taken from every other bed of a cast of pig-iron I find the silicon to vary considerably, the iron coming first from the furnace having the highest percentage of silicon. Additional analyses will be made to determine this point. The following are the silicon results, beginning with the first bed that is filled:

1st Cast.		*2d Cast.*	
1st bed	2.328	1st bed	2.021
3d "	2.058	3d "	1.732
5th "	1.890	5th "	1.741
7th "	1.800	7th "	1.765
9th "	1.834	9th "	1.722
11th "	1.834	11th "	1.783
		13th "	1.853

I also find that the percentage of silicon varies in each pig, being higher at the point of the pig than at the butt. This is shown by the following results:

1.	Point of pig	2.328	Butt of same pig	2.157
2.	" "	2.058	" " "	1.960
3.	" "	1.890	" " "	1.806
4.	" "	1.800	" " "	1.751
5.	" "	1.834	" " "	1.787

Laboratory Crane Iron Co., Catasauqua, Pa.

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NOTES ON THE DETERMINATION OF STARCH.*

By A. L. Winton, Jr., Ph. B.

The determination of pure anhydrous starch in different varieties of commercial starch may be satisfactorily accomplished by heating the substance with dilute hydrochloric acid according to Sachsse's method, determining the dextrose thus formed by Allihn's method, and from the dextrose found, reckoning the starch.

It is claimed that direct heating of the substance with acid is not admissible in the case of potatoes, grains and other agricultural products, partly because cellulose also is in a measure converted into dextrose by acids and partly because the acid dissolves certain ash ingredients which would be afterwards precipitated by alkaline copper solution.

Several methods for separating the starch from such substances have been devised, and it was with the view of learning how they compared with each other as regards accuracy and convenience that the following investigations were undertaken.

ALLIHN'S METHOD FOR DETERMINATION OF DEXTROSE.†

Since in all the methods for estimation of starch which I have tested, with the exception of Asboth's, the starch is converted into dextrose, it is of first importance that the method used for determining dextrose should be trustworthy and properly executed.

Allihn's directions are briefly as follows:

For preparing alkaline copper solutions, two solutions are made up.

Solution No. I. contains 173 grms. Rochelle salts and 125 grms. Caustic potash dissolved in water and made up to 500 c. c.

No. II. contains 34.69 grms. crystallized copper sulphate dissolved in water and also made up to 500 c. c.

60 c. c. of alkaline copper solution prepared immediately before using by mixing 30 c. c. No. I. and 30 c. c. No. II. are heated just to boiling in a beaker of 300 c. c. capacity over a lamp. To the boiling liquid 25 c. c. of dextrose solution

* From Report of the Conn. Agr. Exp. Station for 1887.

† J. prakt. Chem., 22, 52. Ztschr. anal. Chem., 22, 448.

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(containing not more than .25 grms. dextrose) are added and the heating further continued until boiling begins again. After the reduced copper suboxide has settled it is collected on a weighed asbestos filter, washed with cold water (at first by decantation, finally with alcohol and ether and dried at 100° C. The copper suboxide is reduced to metallic copper by heating to redness in a stream of dry hydrogen, and to prevent oxidation is cooled in the same gas. From Allihn's table the weight of dextrose, corresponding to the weight of copper, is found.

For an asbestos filter a Gooch crucible with a thick layer of asbestos may be used, although in my experience the filtering tubes described by Allihn are more convenient and retain the finely divided precipitate better. These are easily made from a piece of hard glass tubing 4 inches long and ⅔ of an inch in diameter by drawing out one end to a small opening and slightly expanding the other. In the narrow portion of the tube a small platinum cone is fitted and a layer of asbestos ½ inch deep is packed in with the aid of a suction pump and a glass rod.

For reducing the copper suboxide the tube is attached by means of a perforated cork to the apparatus which provides a stream of dry hydrogen and after air has been expelled it is carefully ignited in a free flame and cooled before turning off the hydrogen.

In using the method, the following precautions are essential:

I. The solutions for preparing alkaline copper solution must be freshly made and never mixed until immediately before using.

II. After adding the dextrose solution the liquid is simply heated to boiling and *not longer.* 4 minutes boiling brings the result one per cent. or more high.

III. As soon as the precipitate has settled it is collected without further delay on the weighed filter.

IV. Care must be taken that the filter completely retains the precipitate. It is a good practice to let the washings

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stand for some time so that if any of the copper suboxide has run through it may subside. In suspension it is hardly visible.

The above method gave me perfectly accurate results with pure, anhydrous dextrose and was used in all the determinations of dextrose which were made in the following investigation.

ACTION OF DILUTE SULPHURIC ACID ON DEXTROSE.

Since the methods of determining starch involve a treatment with dilute sulphuric or hydrochloric acid it is important to know whether the dextrose formed in the process is itself subsequently changed by the acid.

The experiments of both Allihn and Salomon seem to show that sulphuric acid is poorly adapted for the conversion of starch into dextrose.

The former in an elaborate series of experiments using .1, .2, .5, and 1 per cent. sulphuric acid, and heating under pressure at temperatures from 100° C. to 114° C. was not able under the most favorable circumstances to obtain more than 95 per cent. of the starch in the form of sugar.

Salomon finds the chief difficulty to be in the change into "humus-like" substances which dextrose undergoes on protracted heating with sulphuric acid. Owing to the formation of such substances the solution gradually darkens in color.

50 c. c. of a solution of dextrose which contained 4.678 grms. of the pure dry substance after boiling 4 hours with 20 c. c. of 5 per cent. sulphuric acid was found by him to contain but 4.446 grms. of dextrose, in other words but 95 per cent. of the original quantity. 5 per cent. sulphuric is, however, twice the strength of the acid ordinarily used for this purpose.

Prof. R. H. Chittenden (of Yale Univ.) has found that dextrose is not altered on boiling two hours with 2 per cent. sulphuric acid, still a modification of his method described further on in which the starch was first treated with saliva until the solution gave no reaction with iodine solution, then boiled two hours with 2 per cent. sulphuric acid, gave results which were 1 per cent. low.

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ACTION OF DILUTE HYDROCHLORIC ACID ON DEXTROSE.

Four portions of pure anhydrous dextrose of about 2.5 grms. each were digested with 2 per cent. hydrochloric acid exactly as prescribed by Sachsse's method to be described further on except that the time of heating was varied. After cooling, the acid was nearly neutralized with sodium hydrate, and dextrose determined by Allihn's method.

The following are the results :

	Time of Heating.	*Per cent. of Dextrose.*	*Color of Solution.*
I.	1 hour	100.24	Colorless.
II.	3 hours	100.22	Light straw.
III.	11 hours	96.85	Dark yellow.
IV.	17 hours	94.59	Dark brown.

The solutions which after one hour's heating still remained colorless and after three hours were but slightly tinged with yellow, on further heating soon began to darken in color.

No. I and II show that after three hours heating the dextrose remained practically unchaged, whilst on the other hand III heated 11 hours was found to have lost 3.15 per cent., IV heated 17 hours 5.46 per cent. of the original quantity of dextrose. From these experiments we conclude that the action of 2 per cent. hydrochloric acid on the dextrose as employed in Sachsse's method is not sufficient to appreciably affect the results. Heating longer than three hours brings the results low.

In order to have for experiment starch of known composition a quantity was prepared from potatoes and after being allowed to dry in the air was carefully bottled and used in all the following experiments. In this sample, water, ash, fiber and starch were determined by the methods used by Allihn* and Salomon† as follows :

Water : Two grams were dried to a constant weight at 120° C. in a stream of hydrogen.

Ash : The burning to ash was carried on in a muffle furnace at a heat below redness.

Fiber : The flocks which remained undissolved after con-

*J. prakt. Chem. 22, 79. †J. prakt. Chem. 28, 84.

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verting the starch into sugar were filtered on a weighed filter, dried at 100° C. and weighed.

Starch: By Sachsse's method to be described immediately.

RESULTS OF ANALYSES OF POTATO STARCH.

	I	*II.*	*III.*	*Average.*
Water	15.16	15.18		15.17
Ash	.63	.61		.62
Fiber	.01	.03		.02
Starch	84.55	84.37	84.69	84.54
				100.35

The most approved methods of determining Starch were next tested as follows:

SACHSSE'S METHOD FOR DETERMINATION OF STARCH.

[Chem. Centralbl. 1877, p. 732.]

3 grms. of the air-dry substance are heated in a boiling water bath for three hours with 200 c. c. water and 20 c. c. of a 25 per cent. hydrochloric acid (Sp. gr. 1.125).

The flask is provided with a condenser consisting simply of a long tube one-half inch in diameter attached by means of a perforated rubber stopper. After cooling, enough sodium hydrate solution of known strength is added to nearly (but not quite) neutralize the acid and the liquid is made up to 250 c. c. (or some other convenient volume) and an aliquot portion of 25 c. c. used for estimating dextrose by Allihn's method already described.

The weight of dextrose multiplied by .9 gives the weight of starch, considering its formula to be $C_6 H_{10} O_5$. In the sample referred to, this method gave 84.54 per cent. of starch.

PROF. CHITTENDEN'S METHOD OF DETERMINING STARCH WITH USE OF SALIVA.

The details of this method which have been furnished us by Prof. Chittenden are as follows:

3 grms. of the finely powdered substance are made into a paste of even thickness with 400 c. c. of boiling water. After cooling to 40° C. 15 c. c. of filtered and neutralized saliva are

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added and the temperature kept at 40°* until a drop of the liquid gives no coloration with iodine solution.

For neutralizing the saliva .2 per cent. hydrochloric acid is added drop by drop until the reaction with delicate litmus paper is neutral (the diastatic action of normally alkaline saliva is increased by neutralizing it). An excess of acid must be avoided since .003 per cent. hydrochloric acid almost completely checks the action of the ferment. †

The soluble dextrine and maltose into which the starch has been completely changed, are separated from the insoluble matter by filtering.

The filtrate after concentration to 200 c. c. is treated with hydrochloric acid precisely as in Sachsse's method and dextrose is determined by Allihn's method.

The following results on the potato starch of my preparation were obtained by this method.

	I.	*II.*	*Average.*
	84.45	84.85	84.65
By Sachsse's method . .	. .	. .	84.54

The advantage which saliva as a ferment in starch analysis has over the malt extract usually employed, is that it does not, like the latter, contain soluble carbhydrates which become converted during the process into dextrose.

When, however, a large number of determinations are to be made and it is impossible for the chemist to supply a sufficient quantity of saliva, malt extract must be used. In this case a blank analysis with the malt extract is made by the same process as the others and a correction made.

Malt extract is best prepared by treating 50 grms. of malt with 1000 c. c. of water for 3 hours at 40° C. About 25 c. c. of this extract are equivalent to 15 c. c. of neutralized saliva.

The digestion of the substance in which starch is to be determined with this ferment solution is carried on at 50°–55° C.

To further illustrate the importance of limiting the heating with dilute hydrochloric acid to three hours, three portions of

*Studies from the Laboratory of Phisiolog. Chem. Sheffield Scientific School, for the year 1884–1885, 121.

† Chittenden, l. c., p. l.

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starch were treated by Chittenden's method exactly as described above except that the heating with acid was continued 17 hours.

The results were 3 per cent. low.

	I.	*II.*	*III.*	*Average.*
	81.15	81.88	80.93	81.32
By Sachsse's method	. .	. .	. .	84.54

In the following trials a 2 per cent. sulphuric acid was substituted for a 2 per cent. hydrochloric acid. The solutions of starch in saliva were boiled gently over a Bunsen burner for 2 hours.

Although the color of the solution was quite dark the results are but 1 per cent. low.

	I.	*II.*	*III.*	*Average.*
	83.48	83.61	83.56	83.55
By Sachsse's method	. .	. .	. .	84.54

MARCKER'S EARLIER METHOD FOR DETERMINATION, OF STARCH IN POTATOES.

[Land. Versuch. St. 25-107.]

This method was used by Märcker in the analysis of a large number of samples of potatoes. From the results thus obtained he has prepared his tables for the rough estimation of the starch content of potatoes from the specific gravity of the tuber. This method has been extensively employed for the determination of starch in grains and feeding stuffs.

3 grms. of the finely pulverized air-dry potatoes are heated with 50 c. c. of water for 4 hours at 135°—140° C. under pressure (3–4 atmospheres). After cooling to 90° the starch which has been converted into the soluble modification is separated from the insoluble matter by filtering with the aid of suction.

The filtrate is made up to 200 c. c. and treated with hydrochloric acid as in Sachsse's method. After neutralizing the acid with sodium hydrate, 7–8 c. c. of basic lead acetate are added to precipitate pectin substances, and the liquid is made up to 500 c. c. and filtered through a dry filter. 200 c. c. of the filtrate are made up to 250 c. c. with 1 per cent. sul-

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phuric acid and after the precipitated lead sulphate has settled, once more filtered through a dry filter and dextrose determined in 25 c. c. of the filtrate.

For converting the starch into the soluble modification we have heated the substance, contained in a brass vessel, covered with a tightly fitting lid together with 50 c. c. of water in a Müncke's steam digester.

In using this apparatus care must be taken not to allow the pressure to fall off after digestion so rapidly as to occasion mechanical loss from the violent boiling of the contents of the vessels.

Solution of basic lead acetate is prepared by boiling 155 grms. of lead acetate and 109 grms. litharge with 400 c. c. of water and making the filtrate up to 500 c. c.

Results obtained on the nearly pure potato starch agree with those by preceding methods.

	I.	*II.*	*Average.*
By Märcker's method	84.50	84.77	84.63
By Chittenden's method . . .			84.65
By Sachsse's method			84.54

MARCKER'S LATER METHOD FOR DETERMINATION OF STARCH IN GRAINS AND POTATOES.

[Chem. Zeit. ix, 319.]

[Reprinted Ztschr. anal. Chem. **24**, 617.]

3 grms. of the finely ground substance are heated with 50 c. c. of water to 90° C. and after cooling to 65° mixed with 5 c. c. cold malt-extract (50 grms. of malt extracted with 1000 c. c. water). After digesting ½ hour (at 65° or better at 55°), 10 c. c. of 1 per cent. tartaric acid solution are added and the mixture heated under a pressure of 3 to 4 atmospheres for ½ hour as has been described. When cooled to 65°, 5 c. c. malt extract are again added and after ½ hour the insoluble portion is removed by filtration. The filtrate is heated on a boiling water bath 2½ hours with 15 c. c. of 25 per cent. hydrochloric acid, and enough water to make a volume of 200 c. c.

The acid is then nearly neutralized with sodium hydrate and dextrose is determined by Allihn's method. Märcker

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states that by this method a complete solution of the starch is effected without any appreciable decomposition of the dextrose.

In order to verify this statement and also to study the solvent action of tartaric acid under pressure, 4 portions of potato starch of 2.5 grms. each were weighed out into brass vessels.

I. and II. were treated exactly as has been described with ferment solution and tartaric acid except for reasons before stated 5 c. c. of neutralized saliva were substituted for 5 c. c. of malt extract.

III. was digested directly with 55 c. c. of water and 10 c. c. 1 per cent. tartaric acid. The treatment was the same as for I. and II. except that addition of ferment solution was omitted.

IV. was simply heated under pressure for ½ hour with 65 c. c. of water.

All four were heated (without filtering) with hydrochloric acid as directed, neutralized with sodium hydrate, made up to 250 c. c. and dextrose determined in 25 c. c. From the dextrose the percentage of starch was computed.

I	84.86
II	84.47
III	84.67
IV	84.81

These results indicate that the conversion into dextrose was in each case complete.

After digestion with saliva in I. and II. the starch was only partially in solution, although the diastatic action of 5 c. c. of saliva is greater than of 5 c. c. of malt extract. The quantity of anhydrous starch in 2.5 grms. of potato starch is about the same as in 3 grms. of air-dry potatoes.

The object of this first digestion with ferment solution recommended by Märcker is apparently not to effect complete solution of the starch but to remove the larger part of it so that tartaric acid may act more readily on that which may be enveloped in vegetable tissue.

In III. heated under pressure ½ hour with tartaric acid the

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solution of the starch was complete, whilst IV. heated in the same way with water alone was still milky from undissolved starch.

The addition of .1 grm. of tartaric acid shortens the time of heating necessary for effecting a complete solution of the starch.

The results obtained on pure potato starch by both of Marcker's methods and by Chittenden's method agree with those by direct conversion with acid according to Sachsse's method, and with the result got by difference where water, ash and cellulose were determined.

In each case the starch was brought into solution before the digestion with acid so that if insoluble matter had been present it could have been separated and in each case also the total amount of starch used was obtained finally in the form of dextrose.

COMPARISON OF THESE METHODS OF POTATOES.

It seemed next desirable for the sake of comparative results to estimate the starch in a sample of potatoes by each of these methods. For this purpose a number of sound potatoes were cleaned, weighed, cut into thin slices and dried in a current of warm air. They were then ground rather coarsely, taking care to avoid loss, and after standing exposed to the air several days were again weighed and a subsample was taken and reduced to a fine meal, all of which passed through a bolting cloth.

This air-dry substance amounted to 24.5 per cent. of the fresh sample.

Duplicate portions of three grams of this air-dry potato-meal were treated as follows :

1. By Märcker's earlier method.
2. Same as 1, except that "pectin substances," etc., were not removed by precipitation with basic lead acetate.
3. By Märcker's later method.
4. By Chittenden's method.

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5. By Sachsse's method without separating cellulose, which was filtered out in 1, 2, 3 and 4.

The solutions of dextrose were in each case made up to 250 c. c., and 25 c. c. was used for the determination.

	Per cent. of Starch found in Air-dry Sample.		
	I.	*II.*	*Average.*
1	67.05	66.52	66.78
2	68.60	67.98	68.29
3	69.78, 69.30	69.46	69.51
4	69.30	68.76	69.03
5	71.60	71.64	71.62

It is evident from 1 and 2 that basic lead acetate removes substances which reduce alkaline copper solution; in 2, 3, 4 and 5, however, this was purposely omitted as probably the error in each case would be the same and would not alter the value of the results for comparison.

The results in 5, where the material was digested directly with hydrochloric acid without previous separation of cellulose, etc., are considerably higher than any of the others. These higher results were at first supposed to be due to the partial conversion of cellulose into dextrose by heating with hydrochloric acid. In order to ascertain whether this supposition was correct, the residues which had been separated in 2, 3 and 4, of which those from 2 and 4 had been dried at 100° and weighed, were soaked in water until soft, then ground to a pulp, and finally digested with two per cent. hydrochloric acid for three hours, neutralized, made up to 250 c. c. and the copper reduced by 25 c. c. was determined.

	Reduced Copper.		*Per cent. of starch equivalent to copper.*		*Per cent. of dry residue.*	
	I.	*II.*	*I.*	*II.*	*I.*	*II.*
2 . .	.0010	.0017	. .	. .	5.66	5.70
3 . .	.0019	.0022	. .	. .	Not weighed.	
4 . .	.0099	.0131	1.96	2.56	9.33	10.37

To our surprise the reduced copper in 2 and 3, if added to that obtained from the soluble portion, was not sufficient to make .4 per cent. difference in the results, even if the fact is

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disregarded, that the boiling of alkaline copper solution alone invariably reduces a little copper.

In 4, on the other hand, the reduced copper was equivalent to 1.96 per cent. of starch in I. and to 2.56 per cent. in II. The weights of the dried residues in this case were also much greater than in 2. In 4, the total reducing power of the soluble portion and residue, after treating with acid, nearly agree with that where the sample was digested directly with acid. Thus:

	Reducing Power Reckoned as Starch.		
	4. (Chittenden's saliva method.)		*5. (Direct conversion.)*
	I.	*II.*	
Soluble in saliva . . .	69.30	68.76	. .
Insoluble in saliva . . .	1.96	2.56	. .
Total	71.26	71.32	71.60

What the residues in 4 contained after digestion with hydrochloric acid which reduced alkaline copper solution is not known. Possibly the starch was not completely in solution or the washings may have been incomplete, as the residue was slimy and was washed with difficulty, but it cannot be concluded that cellulose was converted to such an extent into dextrose, since little or no reduced copper was obtained when the residues in 2 and 3 were treated in the same way.

Why the results by either of Märcker's methods are lower than those by direct conversion cannot be explained except by considering that an actual decomposition takes place on digestion under pressure.

Our experiments seem to show that pure starch treated by either of Märcker's methods can be completely recovered as dextrose, but in the case of the potato other substances are present which may themselves decompose or may cause a decomposition of starch. The potato also contains water-soluble matters which reduce alkaline copper solution. From the potato-meal here operated on I extracted by cold water matters, reducing copper which reckoned as dextrose amounted to 3.59 per cent. Having proved that in this particular sam-

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ple of potatoes, the troublesome operations which Märcker employs for removing cellulose previous to digestion with acid are needless, the question arose whether the same would hold true for other samples of potatoes and for the cereal grains and other agricultural products in which it is often desirable to accurately determine starch as a measure of their value for the manufacturer of commercial starch or of alcohol, and also whether it would hold true for pepper in which starch is often determined to decide whether the sample is pure or adulterated.

The following experiments were made to cover these points. Samples of graham flour, maize meal (prepared from the whole kernel), rice (without the hulls), beans and pepper were finely pulverized, and, with the exception of the graham flour, were sifted through bolting cloth.

In portions of 3 grams each, starch was dissolved and separated from the cellulose and other insoluble substances by Märcker's earlier method (digestion with water for 4 hours under pressure of 3–4 atmospheres) and by his later method (digestion with malt extract one-half hour, then with tartaric acid under a pressure of 3-4 atmospheres one-half hour and finally again with malt-extract). The starch solution was filtered off immediately from the residue, which was washed quickly and thoroughly with boiling water, for when starch is simply brought into solution by digestion under pressure with water alone, it is necessary to filter without delay while hot, as starch is precipitated on cooling.

The residues were digested 3 hours with 200 c. c. of water and 20 c. c. of hydrochloric acid (sp. gr. 1.125) and reducing substances in the resulting solutions after filtration were determined in 25 c. c., corresponding to .3 grams of substance, by Allihn's method and calculated as starch when possible. When the weight of reduced copper is less than 10 milligrams, the reducing substance expressed in terms of starch can not be determined by the use of Allhn's tables.

The results appear in the following statement :—

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	Residues from Märcker's earlier method yielded :		Residues from Märcker's later method yielded :	
	Copper	*Equivalent to per cent. of Starch.*	*Copper.*	*Equivalent to per cent. of Starch*
Graham flour . .	.0015	.....	.0000	.....
Maize	.0010	.....	.0017	.....
Rice	.0002	.....	.0008	.....
Potatoes, 1st sam.	.0010	.....	.0022	.....
	.0017	.....		
Potatoes, 2d sam.	.0010	.....	.0019	.....
	.0000	.....	.0022	
Beans	.0060	.92	.0073	1.11
Pepper	.0087	1.33	.0130	1.98

These results indicate that in determining starch, no appreciable error is introduced by omitting the separation of cellulose and other insoluble matters before digestion with hydrochloric acid in the case of graham flour, maize meal, rice and potatoes. In the case of beans and pepper there is a considerable quantity of some copper-reducing material produced by the action of acid on the insoluble matters. Whether this is due to hydration of cellulose does not appear. But in those materials in which *accurate* starch determinations are most desirable the insoluble matters yielded only a minute quantity of reducing substance when heated with acid.

As further evidence, a third sample of potatoes from an entirely different source was put through the process for separating cellulose according to Märcker's earlier method, and the residue digested with acid as before. In this case 12 grams of the air-dry substance was used, so that the 25 c. c. of the solution corresponded to 1.2 grams, or four times what had been used in preceding cases. The weight of reduced copper was but .0016 grams.

We therefore conclude that the simplest and in other respects the most satisfactory method for estimating starch in potatoes and cereal grains, is to digest the air-dry sample directly with a two per cent. hydrochloric acid and proceed in other respects as has been described.

NOTES ON ASBOTH'S METHOD OF DETERMINING STARCH.

[Repert. anal. Chemie. No. 20. Translation in Analyst, xii, 138.]

Asboth has shown that baryta starch $[C_6H_{10}O_5]_4BaO$, first

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prepared by Zulkowsky by the action of baryta water on soluble starch, is also formed and precipitated when baryta water is added to starch which is simply suspended in water in the form of paste.

On this reaction he bases a volumetric method for the determination of starch in cereals which is here copied from the Analyst, vol. xii, page 140.

ESTIMATION OF STARCH.

"Weigh out about three grams of the flour and rub well in a mortar with cold water; but in the case of hard substances like maize, rice, peas, boiling water must be used. Pour off into a 250 c. c. flask, and rub residue again and again with small quantities of water, until the bulk of the starch is removed; finally introduce residue also into the flask. Add water up to about 100 c. c., and heat in water-bath for half an hour, with occasional stirring. After cooling, add 50 c. c. of standard baryta water; cork the flask, and shake well for two minutes. To completely separate the baryta starch, add proof spirit up to the mark. After ten minutes pipette off 50 c. c., but if a flocculent precipitate refuses to settle, filter a portion of the fluid through glass-wool contained in a tube. Titrate the excess of BaO with decinormal hydrochloric acid, using phenolphthalein as an indicator. The interval during the settling of the precipitate I utilized in standardizing the baryta water."

"I use 10 c. c. baryta water. and add 50 c. c. of thoroughly boiled distilled water before checking it." "The difference in BaO between the two determinations was first multiplied by 5, then by 4.235=amount of starch."

"An analysis can be finished in about an hour and a half. I must call attention to the fact that if the liquid is not frequently shaken during the heating, there will be a tendency to form lumps of starch paste which are but imperfectly acted on by baryta water."

I have tried this method on the pure potato starch previously described with the following results:

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	Asboth's Method.	*Sachsse's Method.*
Pure Starch	82.83, 83.02, 83.79	84.54

With pure starch the titration was quite sharp, the color changing with a single drop of acid, but with potatoes, however, the point of neutrality can only be approximately determined, so that although duplicate results made by the same chemist at the same time may agree, it is extremely difficult to decide whether the point of absolute neutrality has been reached or not.

A little difference of opinion on this point would alter the results one or two per cent. Even with pure starch, where the titration was comparatively easy, it is much more difficult to get sharp results than by gravimetric methods. We have also made determinations of starch by Asboth's method in the (air-dry) potatoes sent by Mr. Platt as follows:

	Asboth's Method.	*Sachsse's Method.*
CCXLVI	70.14 70.87	73.81
CCXLVII	74.00 73.60	73.60
CCLIX	72.08 71.69	69.96
CCLX	70.00 70.22	72.40
CCLXI	69.88 70.66	72.07
CCLXII	62.11 63.19 63.62	70.60
CCLXIII	62.97 62.29	70.68

KEROSENE AND GAS AS PROTECTORS OF OXIDIZABLE SOLUTIONS.

By Frank H. Morgan.

Standard authorities on volumetric analysis generally concur in the statement, that a layer of refined petroleum floating on standard solutions protects them from the action of the air.

Mohr, among directions for making a solution of $SnCl_2$ says "eine etwa 10 mm. schichte von Petroleum welche den zutritt der Luft volkommen abschliesst."

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Sutton, in a similar connection states "a layer of petroleum such as is used for burning * * * * places an impermeable division between the air and solution."

I have made quite a number of experiments to determine how valuable this protection is for oxidizable solutions.

The results show quite conclusively that a layer of pure benzene (C_6H_6) or of refined kerosene, 15 to 20 mm. thick, permits the passage of oxygen with considerable rapidity.

A brief description of some of these experiments may be interesting. To avoid unnecessary details I will premise that all of the solutions experimented upon were prepared with great care, free from dissolved oxygen or any oxidizing substance, as shown by tests made in each case several hours after they were under the protecting layer. They were kept in bottles provided with tight-fitting rubber corks carrying tubes for drawing portions of the solution for analysis. They were protected from direct sunlight and not subjected to any considerable variations in temperature.

Exp. A: Nov. 16, 1886; Solution of Ferrous chloride, Iron wire 5 grms.; HCl (1.2) 150 c. c.; H_2O 700 c. c.; protecting layer of C. P. Benzene (C_6H_6) 15 mm. thick. The following analyses show quite rapid permeation of the benzene by oxygen.

Time elapsed.	*Fe'' in 100 c. c. of sol.*	*Loss oxidation in 100 c. c.*	*Per cent. of Original Strength.*
0	0.5735 grm.		
7 days	0.5640 "	0.0095 grm.	98.33 pr. ct.
15 "	0.5459 "	0.0181 "	95.17 "
72 "	0.4525 "	0.0934 "	78.89 "
Total 94 days.		0.1210	

The rate of oxidation per diem calculated from above data is quite regular, being from 1.2 to 1.3 mgr. The titrations were made on 25 to 40 c. c. of solution under protection of CO_2, by $K_2Cr_2O_7$ solution. Volume of solution remaining after last

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analysis was about 500 c. c. This one-half liter had then suffered an oxidation of 0.6050 grm. Fe″ requiring 0.0864 grm. or about 60 c. c. of oxygen.

The inrush of air when exit tube was opened to draw a portion for the last analysis was quite large.

Exp. B: Solution of $FeCl_2$ was made about the same as in Exp. A. and kept under illuminating gas, being connected with gas cock by a rubber tube one-eighth in. in diameter and 3 feet long. From March 28 to May 2, a period of thirty-five days, the solution lost (per 100 c. c.) from 0.5973 Fe″ to 0.5953 Fe″ equivalent to a loss in strength of 0.07 per cent.

Exp. C: Solution of stannous chloride ($SnCl_2$). [Pure tin 50 grms.; HCl (1.2) 250 c. c.; H_2O 750 c. c.]

This solution was divided, one-half being protected by a layer of pure kerosene 30 mm. thick, the other by gas as in Exp. B.

In a month's time, the solution covered by kerosene had formed a heavy deposit of $SnOCl_2$, while the solution under gas had oxidized only slightly.

Exp. D: Solution of stannous chloride ($SnCl_2$). [Pure tin 75 grms.; HCl (1.2) 300; H_2O 1200.]

Solution placed in a dark yellow green bottle of three liters capacity, provided with tubes for drawing samples and connecting with gas cock, and with a funnel tube with glass cock for subsequent running in of kerosene. This solution was protected by gas alone for fifty-six days, then by kerosene* sixty days, then by gas and kerosene for 167 days with results as follows. The strength of solution is stated in terms of its reducing power on Fe‴†. The loss=per cent. is of streng that beginning of each period.

*Acmé Brand.

†I use Fe″ and Fe‴ to indicate ferrous and ferric iron respectively.

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Solution under Gas 56 Days.

Analyses.	*1 grm. sol. reduces.*	*Loss per 1 grm. sol.*	*Loss—per ct.*
April 1.	0.04460 Fe'''		
May 26.	0.04436 "	0.00024 Fe'''	0.53 pr. ct.

Solution under Kerosene 60 Days.

July 25.	0.03697 Fe'''	0.00739	16.65 pr. ct.

Solution under Kerosene and Gas 67 Days.

Oct. 1.	0.03600 Fe'''	0.00097 Fe'''	2.62 pr. ct.

Under Kerosene and Gas 100 Days longer.

Jan. 9.	0.03592 Fe'''	0.00008 Fe'''	0.22 pr. ct.

N. B.—The conclusions from this experiment are very positive; the oxidation that took place during the first 67 days under gas and kerosene was probably due to oxygen contained in the kerosene when the gas was let in July 27th.

Exp. E: Solution of stannous chloride ($SnCl_2$) dilute. [Pure tin 10 grms.; HCl 1.2 200 c. c.; H_2O 800.]

Solution was divided, 500 c. c. being placed in a white glass (1 liter) bottle and marked Ea. Other 500 c. c. was placed in a brown glass bottle marked Eb. Both bottles were connected with gas-cock as in Exp. B.

(Ea) After 72 days, loss of strength=11.13 per cent.

(Eb) After 72 days, loss of strength=10.92 per cent.

A layer of pure kerosene (15 mm.) was then run on to each.

(Ea) was disconnected from gas cock and left with a slight ingress for air into upper part of bottle.

(Eb) was left under gas and kerosene, but gas-cock accidentally closed at an unknown time.

After 70 days.

(Ea) was completely oxidized to $SnCl_4$; loss 100 per cent.

(Eb) had oxidized about same as before; loss 10.47 per cent.

Exp. F: Stannous chloride ($SnCl_2$), under kerosene. [Pure tin 50 grms.; HCl 250; H_2O 250.]

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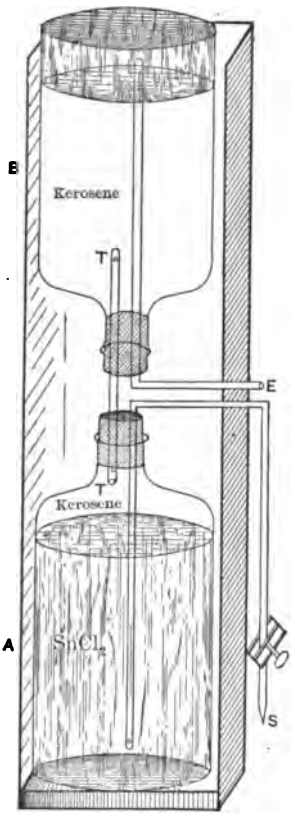

This experiment was devised principally to ascertain whether the oxidation in other experiments was due to any action of the kerosene itself. By use of the apparatus shown in the figure the solution was in contact with the kerosene as in previous experiments, but the diffusion of air or oxygen through the kerosene was rendered nearly impossible. The arrangement is easily understood without a detailed explanation. Bottle A being filled with kerosene, the solution of $SnCl_2$ was forced in through S and gradually displaced the former, which passed through T into bottle B, air passing out by E. As T opens into B by a very small hole in the side of the tube, passage of air by diffusion from upper part of B down to the $SnCl_2$ solution must be very slow indeed. The solution was used for several analyses during the interval.

Analysis Oct. 10, 1887; 1 grm. sol. = $\begin{cases} (a)\ .09156\ Fe''' \\ (b)\ .09168\ \text{"} \end{cases}$

Analysis Jan. 5, '88; (after 90ds.) 1 grm. sol. = $\begin{cases} (a).09168\ Fe''' \\ (b).09177\ \text{"} \end{cases}$

Therefore no oxidation has taken place.

Conclusions: 1. I think these experiments prove that refined petroleums permit a comparatively rapid diffusion of oxygen. 2. Pure kerosene has no deleterious action on strongly acid $SnCl_2$ solutions. 3. Illuminating gas is not a perfect protection for oxidizable solutions, though far better than a thin layer of kerosene.

The method of testing the $SnCl_2$ solutions including the use of a new indicator for reduction of $FeCl_3$ by $SnCl_2$ will be described in the following paper.

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NEW INDICATORS IN THE REDUCTION OF FERRIC CHLORIDE BY STANNOUS CHLORIDE.

By Frank H. Morgan.

I. Blue Flame Indicator.—In the experiments of the preceding paper, a rapid and exact method of determining the strength of $SnCl_2$ solutions was desired. The method by iodine and thiosulphate, in alkaline solution, was rejected on account of the frequent restandardization of the solutions which it required. The method by reduction of $FeCl_3$ seemed most available, provided a direct indicator could be found. The method of Fresenius, using iodine and thiosulphate in getting the end-point of the reduction, was rejected on account of its length and the solutions required. The change from yellow to colorless solution, as indication of the completion of the reduction, is not sharp enough to use in accurate work—it varies too much according to conditions of concentration, etc. It occurred to me that, if a blue color could be produced in the solution, the change from the green caused by the blue and yellow, to pure blue at the point of complete reduction, would form a very good indicator of the end of the reaction. Potassic ferricyanide, under the required conditions, yields a pure blue color, but is more or less quickly decomposed by the boiling strongly acid solution. A number of coal-tar dyes were then tried, but without success. A drop of a very dilute solution of gold chloride, put in after a part of the reduction and consequent formation of $SnCl_4$ had taken place, leaves, at the moment of complete reduction, a violet color (purple of Cassius) which is permanent on boiling. This end-point is, however, too sensitive to varying conditions—the presence of any suspended matter appears to precipitate it. Immersion of the flask in a blue solution proved unsatisfactory. While trying this method, however, it was noticed that the pale blue Bunsen flame, when seen through the solution containing only traces of unreduced $FeCl_3$, had a decided green color, but at the moment of complete reduction it appeared pure blue.

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A few careful quantitative tests of the accuracy of this indicator were conclusive as to its practicability and possible accuracy. After an experience in its use for nearly 100 determinations during the past year, I can say without hesitation that it is a reliable and accurate indicator. It is not an exceedingly delicate indicator, but, as will be seen, is the more practicable.

The following comparison with the change from yellow to colorless solution was made.

Ex. 1. 50 c. c. of H_2O and 25 HCl (1.2) were placed in a 150 c. c. flask and boiled, then one drop of $FeCl_3$ solution, containing .00005 grm. Fe''' was added. After boiling one minute, the solution had a decided yellow color; the blue flame seen through the solution had a pale green tint.

Ex. 2. To the same amount of water and acid as before, a drop of $FeCl_3$ solution containing .00001 grm. Fe''' was added; after one minute of boiling the liquid had a pale but decided yellow tint; the blue flame did not show any green color until another drop of the same $FeCl_3$ solution was added.

Conclusions.—The blue flame cannot detect with certainty less than .00005 grm. of Fe''' in 75 c. c. of water, or about 1 part in 1,500,000. Fairer and more practical tests of the delicacy and accuracy of the blue flame indicator, are those in which a comparatively large amount of $FeCl_3$, $SnCl_4$ and other salts (colorless) are present in the solution, because these are the ordinary and possible conditions in analysis.

Such solutions often have a decided greenish tint, even when an excess of $SnCl_2$ is added, but these green colors do not affect the appearance of the flame.

The following precautions are to be taken. See that the lamp gives a pure blue flame, or what is ordinarily called colorless. Use a small flame, bringing the lamp within one-half inch of the bottom of the flask, but no nearer, else green flames may be produced from the copper in the lamp tube. The

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flask should be of white glass, round bottom, (or Erlenmeyer's) and so clean that the condensing steam shall run down the sides without fogging. The titration may be done in a darkened room, or a dark corner of the hood, or, as I have proved practicable, in the shadow formed by piling several small boxes about the flask, on a table not in direct sunlight.

The following are a few examples of many closely agreeing determinations using this indicator.

May 26, 1887. Determination of strength of $SnCl_2$ solution. (Ex. E, preceeding paper.)

Standard solution $FeCl_3$, 1 grm. = 0.02564 grm. *Fe'''*.

No.	*$FeCl_3$ taken.*	*$SnCl_2$ required.*	*Val. of 1 grm. $SnCl_2$ obtained.*
(a)	27.9816 grms.	16.1566 grms.	.04442 grm. Fe'''
(b)	28.3559 "	16.3924 "	.04436 "
(c)	18.5470 "	10.7230 "	.04436 "
July 25.	Test of same solution $SnCl_2$.		
(a)	8.2516 grms.	5.7191 grms.	.03684 "
(b)	23.3445 "	16.1250 "	.03698 "
(c)	25.7787 "	17.8100 "	.03697 "

N. B.—In these analyses the $SnCl_2$ solution was used as the reagent in the burette-flask,* under gas. By drawing out the jet of the burette to a slender tube, drops about $\frac{1}{50}$ c. c. in size could be obtained. The $FeCl_3$ solution was also weighed for greater accuracy. The titrations were made in a 100 c. c. Erlenmeyer's flask held in the hand by a wooden clamp.

The advantages of the blue flame indicator may be summed up as follows:

(1) It affords a positive end-point, the gradual change of color indicating its approach; by allowing the flame to reach just above the solution for a moment, on the side of the flask opposite to the eye, the contrast between the portion of the flame seen above, and that seen through the solution, gives a very delicate test of the completeness of the reduction.

(2) By its use analyses may be made at night.

(3) It is not affected by a green color in the solution.

* Described in this Journal, Vol. II, p. 1.

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(4) It is not affected by any chemical reactions that do not produce yellow colors.

Cobaltous Chloride ($CoCl_2$) *with strong HCl.*

F. P. Venable† suggested the use of cobalt nitrate to which strong HCl has been added as a delicate indicator for $FeCl_3$.

A. C. Campbell‡ has shown very truly that cobalt chloride rather than the nitrate is the proper reagent.

Neither of these gentlemen seem to realize the true character of the indicator.

The former, without adducing any experimental proof, intimates that the green color is not due to physical mixture of blue and yellow colors in solution.

The behavior of this indicator in a number of analyses tending to show that Mr. Venable was wrong in this opinion, I made the following experiments to test the matter :

I dissolved 5 grms. of pure $CoCO_3$ in 100 c. c. of HCl (Sp. Gr. 1.2) and used this solution in the following experiments :

(1) Took 2 c. c. $CoCl_2$ sol. in a test tube (a) and 2 c. c. HCl in a second tube (b). Added to each tube one drop of HNO_3 (conc).

(a) Color did not appear to change ; but after 3 or 4 minutes a thin layer (by inclining tube) appeared greenish blue.

(b) In 3 or 4 m. had acquired a very pale straw tint.

(a) On being heated quickly changed to yellow.

(b) On being heated became a decided yellow.

Inference : Green color in (a) due to action of HNO_3 on HCl giving a yellow color, which with the blue produces green.

(2) 2 c. c. of $CoCl_2$ sol. was carefully evaporated to dryness, 2 c. c. of water added and again evaporated ; residue dissolved in 2 c. c. of water, and one c. c. of HNO_3 added, no green color produced by boiling.

(3) $CoCl_2$ sol. on addition of $PtCl_4$ solution at once turned green.

† This Journal I, 312. ‡ Ib. II, 4.

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(4) $CoCl_2$ sol. on addition of $K_2C_2O_4$ solution at once turned green.

N. B.—All other green solutions tried, produced the same effect, except some aniline dyes, which were either destroyed, or changed to red by the strong acid. These experiments seem sufficiently convincing proof that the green color obtained with $CoCl_2$ (HCl) and $FeCl_3$, is a physical, and not a chemical phenomenon.

Mr. Campbell suggests this blue $CoCl_2$ sol. as a qualitative reagent for HNO_3.

The above evidence, and indeed Mr. Campbell's own experiments and suggestions show, that it is rather an indicator of any reaction, by which a yellow color is produced without destroying the blue of the $CoCl_2$.

The $CoCl_2$ (HCl) has an advantage over the blue flame indicator, of being more convenient in the day time, and under certain conditions of being a little more sensitive, but has the disadvantage of being affected by a green color in the solution, rendering the end-point under certain conditions uncertain. I have found this to be the case in using it as an indicator in determinations of N_2O_5 in nitrates. In a future paper on the latter subject I will endeavor to explain this point more definitely.

The following analysis of a limonite illustrates the accuracy and agreement of these indicators. Limonite 6.8485 grms. was decomposed by 200 c. c. HCl, filtered and diluted to volume of 500 c. c.

Standard $SnCl_2$ sol. 1 c. c. = .02244 gr. Fe'''.

The following titrations were made on 100 c. c. portions of above solution, in a long necked 500 c. c. r. b. flask ; 25 c. c. HCl and 25 c. c. H_2O being added to each and solution boiled 3 to 5^m before $SnCl_2$ was added.

Blue Flame as Indicator.

$$\left.\begin{array}{ll}\text{(a)} & SnCl_2 = 25.65 \text{ c. c.} \\ \text{(b)} & \text{"} \quad = 25.66 \text{ "}\end{array}\right\} = 42.02 \text{ per cent. Fe.}$$

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$CoCl_2(HCl)$ as Indicator.

$$\left.\begin{array}{ll}(a) & SnCl_2 = 25.70 \text{ c. c.} \\ (b) & \text{"} \quad = 25.69 \text{ "}\end{array}\right\} = 42.08 \text{ per cent. Fe.}$$

The same limonite analyzed by the bichromate method gives as average of many analyses 42.10 per cent. Fe.

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ABSTRACTS.

APPARATUS AND REAGENTS.

Water Blast for Laboratories.—A. Beutell, Chem. Ztg. 11, 1381, claims that the combined water blast and filter pump which is commonly used in laboratories, is unsatisfactory, and he has prepared a water blast which is described as follows:

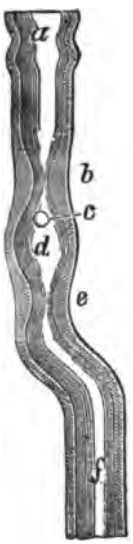

Fig. 1.

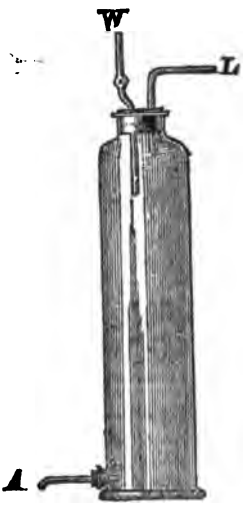

Fig. 2.

Fig. 3.

Fig. 1 represents the pump, a glass tube 6 cm. long with the internal diameter at *b* diminished to 2.5 mm. and at *e* to 3 mm. The space between these points at *d* is slightly enlarged and a small opening is made at *c* for the admission of air. The tube is bent between *e* and *f* to prevent the air from

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passing back again. Fig. 2 represents a 1.5 litre bottle with a two-holed cork in the neck. Through one of these holes the pump *W* is secured and the other contains a bent tube *L* which leads to the blast lamp.

The water enters at *a*, Fig. 1, and passes through the pump into the bottle, Fig. 2, which is kept about two-thirds full. The height of the water in the bottle, and consequently the strength of the blast, is regulated by the size of the discharge pipe *A*. To vary the strength of the blast a regulator, Fig. 3, is made by dividing the discharge pipe in two pieces *AA'* and connecting them with rubber tubing. The internal diameter of the pipe *A'* is slightly diminished. A piece of glass rod *G*, drawn out to a point at one end and flattened at the other end so that the edges touch the walls of the rubber tubing, is placed between the parts of the discharge pipe *A* and A' and by simply moving this in or out the flow of water is easily regulated. S. C.

Apparatus for Filtration.—F. Allihn, Ztschr. anal. Chem. **26**, 721. The funnel is ground into the neck of a flask made of heavy glass provided with a side opening, which can be connected with a filter pump. In the apparatus figured the neck of the funnel is swelled out so that a flask with large neck can be used.

Improved Bunte Gas Burette.—Chem. Ztg. **11**, 1225. Greiner and Friederich's by attaching one of their stop-cocks* to the upper end of Bunte's burette have decidedly improved it. The stop-cock is attached to the upper end of the burette, and, in one position, communicates with a small stoppered tube to contain the reagent, in the second position with the outside air.

Evaporation of Ammoniacal Solutions.—F. Muck, Ztschr. anal. Chem. **26**, 599. Strong ammoniacal solutions cannot easily be evaporated on the water bath without danger of loss from frothing. The author conducts the evaporation as follows: Concentrated sulphuric acid is poured into an evapora-

* See this Journal **1**, 316.

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ting dish and over it, in a crucible resting on a glass tripod, is placed the ammoniacal solution. The dish is covered with a glass plate and heated gently when the evaporation takes place without frothing, the ammonia combining with the sulphuric acid.

Apparatus for Collecting Gases from Mineral Waters.—C. Reinhardt, Ztschr. angewandte Chem. 1888, 1, 48. The author describes two forms of apparatus for this purpose shown in the cuts figs. 1 and 2. Fig. 1 is a brass tube sharpened at the lower end and closed above with the brass tube *c*; *a* is connected with the absorption apparatus and *b* with a hydrogen generator, by means of rubber tubes closed with screw clamps. The tube is now thrust through the cork of the bottle containing the mineral water, turning towards the right until the side opening *e* is below the inner edge of the cork, when the pinch cock on the tube connected with *a* is opened and the gas allowed to pass into the absorption apparatus. The gas remaining in solution is expelled by passing hydrogen through the tube *b*. When the operation is finished *c* is disconnected and the pellet of cork forced out with a glass rod.

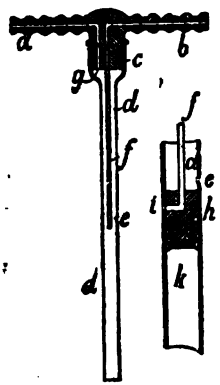

Fig 1. Fig 2.

Fig. 2 is like fig. 1 above, except that *c* is soldered, instead of being screwed to *d*. At *h* a solid piece of brass is soldered having an opening *i* connected with *f*. The lower part of the borer *k* unscrews, so that the piece of cork may be pushed out. Both forms can be obtained of C. Gerhardt, Bonn.

Apparatus for the Estimation of Nitric Acid.—Dr. Kratschmer, Ztschr. anal. Chem. **26**, 608. This is intended for use in Schlösing and Schulze's method, and consists of a flask provided with a stoppered funnel tube and bent delivery tube. Over the delivery tube a cork is slipped, so that it may be handled without burning the fingers. The air is driven out by boiling the water and the small amount in the stem of the

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funnel tube by opening the top for a short time. A boiling solution of ferrous chloride in hydrochloric acid is then poured in through the funnel tube and the boiling continued until no more gas is given off. The gas is collected in the usual way.

Convenient Method for Obtaining Pure (Arsenic Free) Sulphuretted Hydrogen.—Clemens Winkler, Ztschr. anal. Chem. **27**, 26. 100 parts heavy spar, 25 parts coal powder, and 20 parts common salt are finely powdered, and intimately mixed with addition of enough water to make the mass cohere. The mass is made into balls, which are placed in a crucible. Some coal powder is placed over the balls, which are dried slowly, the crucible is then luted, heated to whiteness and cooled rapidly. When the crucible has cooled it is inverted and the material falls out as compact sintered balls which may be broken up with a hammer. The barium sulphide must be kept in tightly closed vessels, and is best decomposed in Kipp's apparatus with HCl.

The Use of Asbestos in Filtering, Especially in Digestion Experiments.—W. Fresenius, Ztschr. anal. Chem. **27**, 32. Solutions which are obtained in determining the digestibility of the albuminoids often give turbid filtrates when filtered through paper. This can be avoided by shaking such solutions with fine asbestos and allowing the mixtures to settle. The clear fluid is then drawn off by means of a siphon. The sediment is washed by adding water two or three times and allowing to settle as before. The residue is finally filtered through a funnel containing a plug of asbestos; if the first portion runs through turbid it is poured back into the funnel. After the residue has been dried the nitrogen in it is determined by Kjeldahl's method.

Apparatus for the Examination of Generator Gas and Water Gas.—F. Fischer, Ber. **20**, 2551. The working tube *A* and measuring tube *M* are filled with mercury by raising the flasks *F* and *L*. This is done most conveniently by opening *h* and *d* and filling *M* first, then closing *h* and turning *d*

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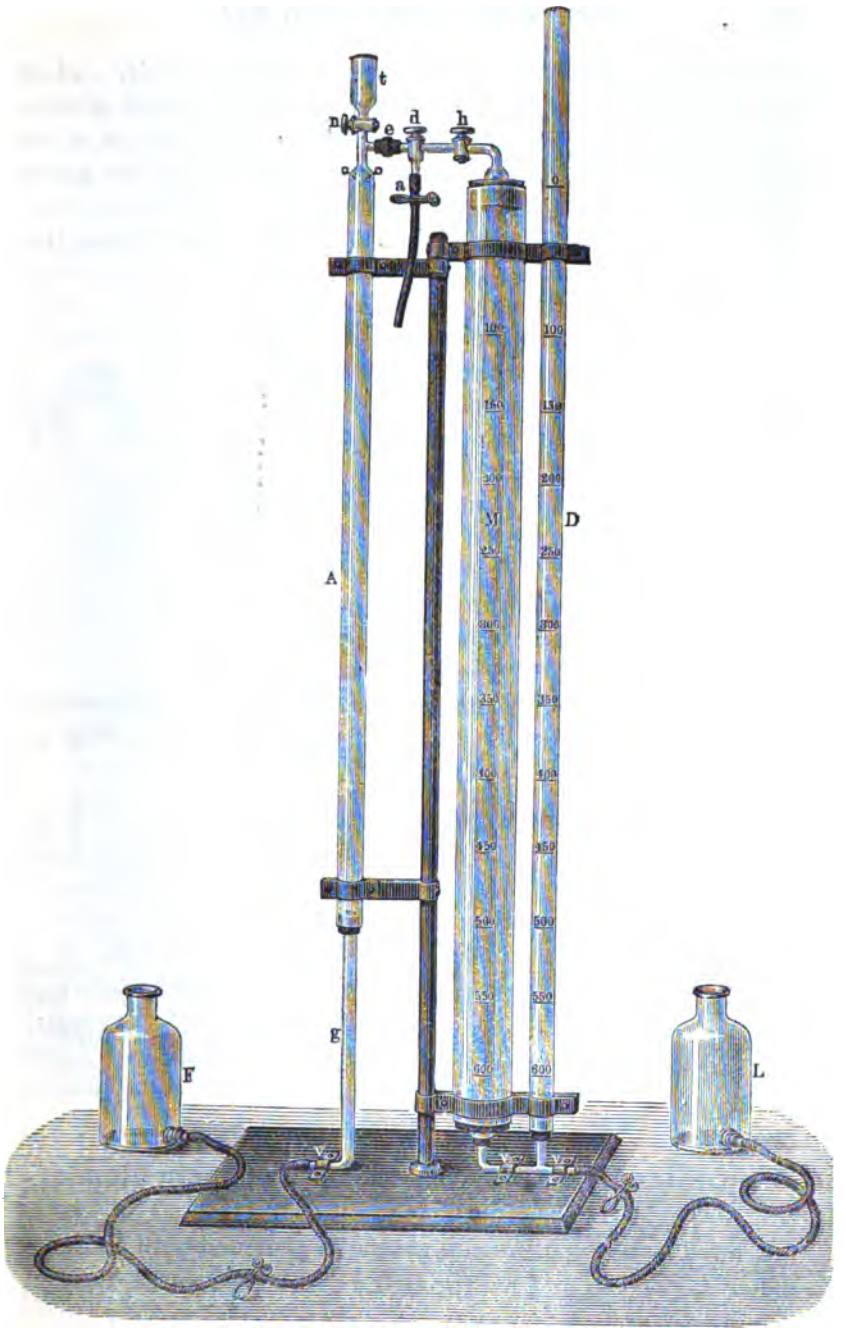

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so that there is communication between tubes *a* and *A*. *A* is now filled with mercury to *e*; the funnel *t* is filled with water, and all but a few drops of this run through *n* and out at *a*, so that *a* is completely filled with water. The end of the glass bulb containing the gas to be examined is now thrust in *a*, the end of the tube broken off within the rubber tube, the other end of the bulb dipped in water and the gas drawn into *A* by lowering *F*. From *A* it is driven over into *M*. Any excess of gas in A and the water is then driven out through *h*. 0.8—1. c. c. of caustic potash solution is now run into *A* and the gas driven over, and, after the CO_2 is absorbed, driven back into *M* until the caustic potash reaches *d*, and the volume again read off. About 0.5 c. c. pyrogallic acid solution is now run in through *t* and the gas brought in contact with this, to absorb the oxygen, and again measured. To determine combustible gases the tube *a* is first cleaned by pouring in water through *t* and running it out at *a*, then some electrolytic oxygen is passed in at *a* and the proper amount passed into *M*, the excess being rejected at *a*. The mixture of explosive gases is then brought into *A*, the spark passed and the contraction determined in M. and the CO_2 formed absorbed as before.

Valve for Wash Bottles.—A. Beutell, Chem. Ztg. **12**, 53. This is designed to prevent the longer tube of the wash bottle from emptying itself after each operation, and is shown in the cut. The tube is partly closed below by holding it in the flame of a Bunsen burner. The glass valve is made by holding a piece of thin, drawn out tube in the flame, until the end has melted to a round ball of glass. After inserting the glass ball, the tube is contracted above it as shown in the figure.

Apparatus for the Determination of Sulphur in Illuminating Gas.—H. Drehsmidt, Chem. Ztg. **11**, 1382. The gas is measured by an experimental gas meter provided with a micrometer stop cock, and led through a glass tube to the Bunsen

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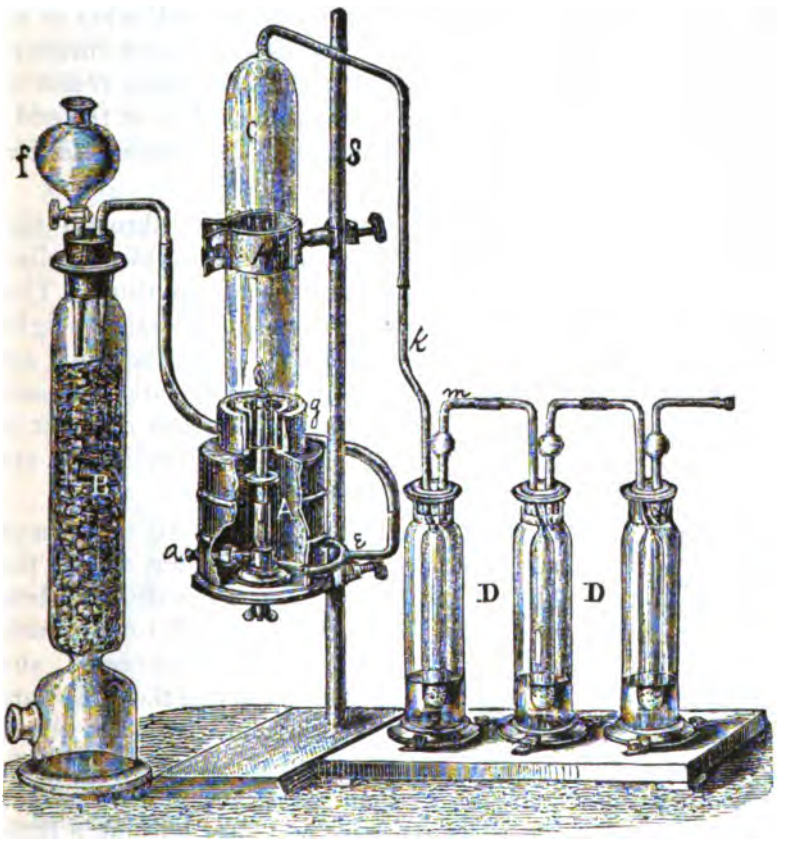
burner in the case *A*. This burner is one of the ordinary type, provided with a cap of wire gauze to prevent the gas from burning in the tube. The pipe *a* of the burner is soldered firmly into the side of the case *A* and is connected with the glass gas conductor by a short piece of rubber tubing. The case *A* is in two parts and made so the upper part fits on



the lower by a beveled joint. A forked tube *e* is fitted in the lower part through which the air is supplied for combustion. This tube is connected by means of rubber tubing, with the wash bottle *B* filled with pumice stone which is kept moist with caustic potash or alkaline lead solution dropping from the funnel tube *f*. The burner tube projects about 1 cm.

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above the top of the case *A* and around this is a circular trough *g* filled with mercury into which the glass cylinder *c* dips. The cylinder *c* is 5 cm. in diameter and 32 cm. long. It is held in position by a brass clamp *H* which is tightened around the cylinder by means of a screw. A glass tube is melted in the top of *c* and is bent downwards to connect with the tube *K*. The ends of these tubes are ground into each other so as to make a perfectly tight joint. The tube *K* passes through the ground glass stopper of the absorbtion cylinder *D* and is then enlarged, as shown in the cut, and sealed up at the end. A row of holes is bored in this tube near the bottom to allow a passage of the gases.

Another tube *m*, containing a bulb, passes through the glass stopper and connects with the second absorbtion cylinder; and this in like manner connects with the third. The connecting tubes of these cylinders are all the same height and the ends are ground to fit each other. Over the joints are placed short pieces of rubber tubing and they are made air tight by the aid of glyerin. The last absorption cylinder is connected with an air pump. These three cylinders are secured firmly to a board with screws.

To make the analysis, 20 c. c. of a 5 per cent. solution of potassium carbonate are placed in each cylinder, and to the contents of the first and second cylinders a few drops of bromine are added to oxidize the sulphurous acid to sulphuric acid. The absorption cylinders are then connected and screwed fast to the board. The cylinder *C* and the case *A* are clamped to the stand *S*, but not connected with each other. *A* is connected with the gas pipe and the wash cylinder *B*. The absorption cylinders are then connected with *C* and the air pump. The gas is then lighted and after burning a little while in the open air the case *A* is turned under *C* and raised until the latter dips into the mercury; at the same time a note is made of the position of the indicator on the gas meter.

The pump is then started by which the supply of air is regulated in order to have complete combustion.

The temperature of the gas is taken by hanging a ther-

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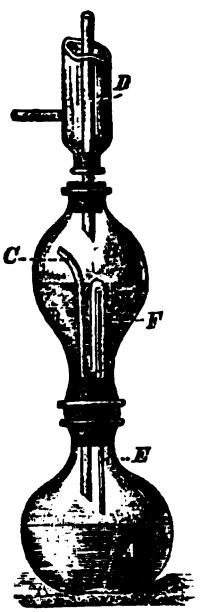
mometer in the gas meter. For an accurate estimation of sulphur 50 litres of gas are used. After the operation is complete the parts of the apparatus are separated from each other by first lowering *A*, removing *C*, and then unscrewing the absorption cylinders. The contents of the cylinders *C* and *D D* are washed into a beaker, acidified with hydrochloric acid and heated to drive off the bromine. The sulphur is then precipitated with barium chloride and weighed in the usual manner. The quantity of sulphur found is calculated to the amount in 100 c. c. of the gas at 10° C and 760 mm. barometric pressure. S. C.

A New Extraction Apparatus.—Paul Bœssneck, Chem. Ztg. **11**, 1600, describes a modification of Rempel's apparatus* as follows:



The flask *A* is connected with the extractor *B* by a good two-holed cork. *A* has a capacity of 500 c. c. and *B* 350 c. c. The diameter of the neck of the extractor is 45 mm. The tube *C* through which the vapor of the extracting liquid is allowed to pass into *B* has a diameter of 1 cm. It is wide enough to allow any of the liquid that may condense in the tube to run back into *A* without checking the flow of the vapor. The upper end of the tube is bent to prevent its being stopped up by the material to be extracted. The vapor of the extracting liquid is condensed by the inverted condenser *D* and percolates through the material to be extracted to the neck of the extractor where it is siphoned through the narrow tube *E* back into *A*. The tube *E* is somewhat larger above the cork and is bent downward, with the end cut obliquely as shown in the cut. This end contains a loose wad of cotton. When the fluid in *B* reaches the

* Chem. Ztg. **11**, 936. This Journal **2**, 76.

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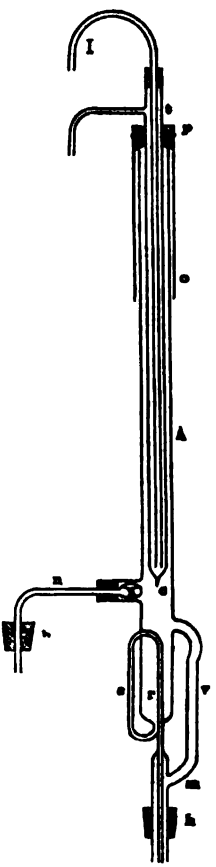
top of the tube *E* it flows back into *A*, drawing off the most saturated part of the extracting liquid until the extractor is emptied. The quantity of liquid in the extractor can be easily regulated by raising or lowering the tube *E*. When extracting with ether a tube open at the top must be used instead of the siphon so the flowing of the liquid into *A* will be gradual.

The advantages of this apparatus over Rempel's as claimed by the author are, greater simplicity, periodic extractions, and separate tubes for the extracting material to *B* and the extract to *A* so that mutual disturbance is completely avoided. S. C.



A Modified Form of Soxhlet's Extractor.—W. H. Kent, J. Am. Chem. Soc. **9**, 182. The extractor is attached to a support by a clamp at A. The condenser t is held in place by the cork p and the tube o, and c is centred by a wooden wedge inserted between o and A. The substance to be extracted is placed in a tube and lowered into r by means of a white thread, previously treated with ether. During the extraction this thread hangs over the tube A and out under the tube o. When the extraction is finished the spoon b is pushed under c and the condensed ether drops down into it and runs out into another flask attached to b. The flasks used all fit the same cork and the corks b and h are of the same size. The author prefers asbestos as the material for drying the milk and follows the plan recommended by Dr. Babcock. (2d Ann. Rep. N. Y. Agr. Exp. Sta., p. 168.)

Modification of Traube's "Capillarimeter."—H. S. Elsworthy, J. Chem. Soc. **53**, 102. The author proposes a modi-

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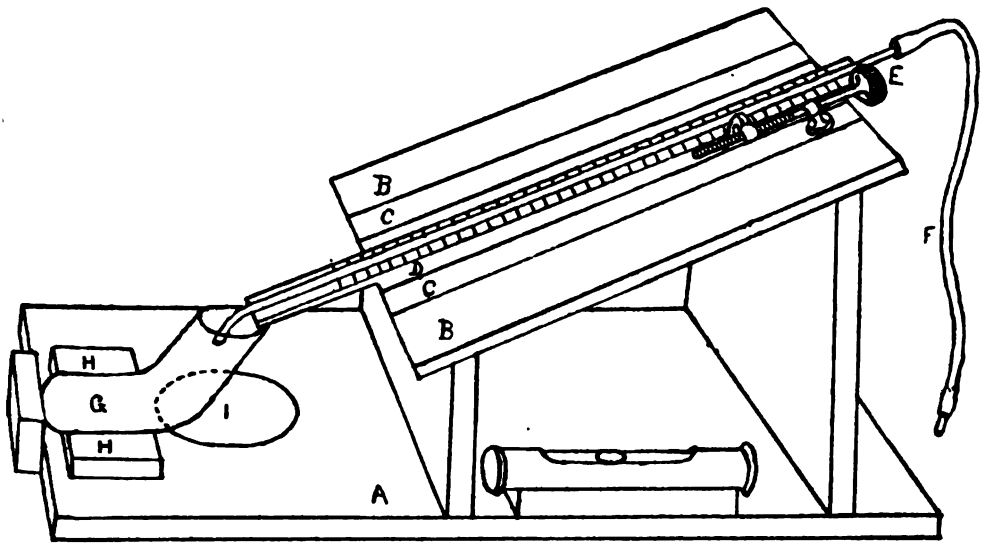
fication of the apparatus used in the capillarimetric method of determining fusel-oil in liquors, as explained by J. Traube in Zeit. für Spirit. Ind., No. 36 of 1886. (See this Jour. Vol. 1, page 108). By using an apparatus made from the thin-walled tube of a broken thermometer, the scale of which is pretty accurately divided into 1.12 mm.; that is, 88.5° equals 100 mm., it is possible to read to $\frac{1}{50}$ per cent., but it can not be accomplished very readily, as the scale has to be adjusted to the surface of the liquid with the greatest nicety. In the following apparatus the rise of the liquid is aided by laying the



tube at an angle more nearly approaching the horizontal. A broken milk scale thermometer, graduated up to 600° F, each division nearly corresponding to 1 mm., that is, 151° equals 150 mm., will answer the purpose for a capillary tube.

On a stand, A, about 15 inches long, is placed a sloping piece of wood, B, the lower end of which is raised 2 inches above the stand, and slants upward at an angle of 10°. In the centre of this is placed a piece of wood, D, made to slide easily between two strips, C C, and to this is attached the scale and tube, the end of the latter being slightly bent down-

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ward. The slide is adjusted by the screw E. On the stand, near the lower end of the inclined plane, is placed a piece of glass tube, G, bent to a convenient angle and ground off level, this being filled with the spirit to be tested. This tube is held in position by two small cork blocks, H H. The scale must be adjusted accurately to the same point each time, and this is effected by bringing the lower end of the scale itself, or a point attached to it, into exact contact with the surface of the liquid. The adjustment can be made more accurate by placing a polished metal or glass reflector, I, under the bent portion of the tube; the exact moment of contact can then be easily observed. The stand should be set exactly level by means of an adjusting screw and a spirit-level, K. An india-rubber tube, F, is convenient for sucking or forcing the liquid through the tube. It can also be used for cleaning the tube with pure spirit.

The sensitiveness of this instrument is about three times as great as that of Traube's. In the latter the rise of a pure 20 per cent. vol. spirit is said to be 50 mm. In the modification a pure spirit rises 173 mm., and with 1 per cent. of fusel-oil, the meniscus is lowered 25 mm. against 7 mm. in Traube's apparatus. The most accurate readings can be obtained by drawing the liquid up the tube 5 or 6 times, and finally to a fixed point 10° or 20° above the point reached by the pure spirit. Since the ethers have a considerable influence on the capillary rise, it is necessary to distil them off from the substance under examination, with soda or potash, before using the apparatus. The amount of dilution required by a proof spirit is one drawback. If, for instance, the original liquid was proof, and contained 0.1 per cent. of fusel-oil, it would require approximately 1½ times its volume of H_2O, and the per centage of fusel-oil in the mixture would be correspondingly lowered. But the experiments with this apparatus show that the use of the capillarimetric method, as recommended by Traube, will tend to a greater accuracy in the determination of fusel-oil, than has as yet been possible. W. W. D., JR.

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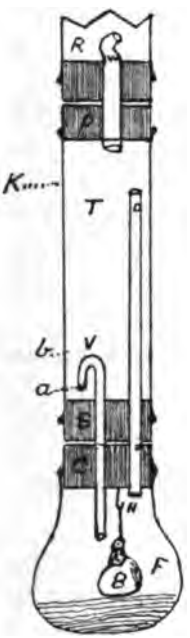
Apparatus for Fat Extraction.—O. Foerster Ztschr. anal. Chem. **27**, 30. The flask A contains 50–70 c. c. B is 30 mm. wide and 190 mm. long, and is ground into A. C, the extraction vessel, is 150 mm. long and 22 mm. wide and is drawn out below in a tube 4–5 mm. wide. The condenser is 140 mm. long, and is ground into B.

An Improved Modification of Soxhlet's Apparatus.—J. J. Barlow, Chem. News, **57**, 56. The apparatus consists of a flask F of about 220 c. c. capacity with a cork c pierced with two holes. The small cotton bag B, containing the substance to be treated, which must be at least one-half inch from the bottom of the flask, is suspended by a platinum wire from the hook H. T is a tube about 7 inches long and 1¼ inches in diameter, closed at both ends by corks P and S, the latter of which is pierced with two holes similar to c. W passes through cork P into condenser R.



The tube D is about 6½ inches long and ¼ inch internal diameter, while the siphon tube V is about ⅛ inch internal diameter.

From 2 to 6 gms. of the substance are taken. About 120 c. c. of ether are put into the flask, which is placed in a beaker of water kept at the temperature of boiling ether. The vaporized ether passes through D into the condenser, is condensed, and collects at the bottom of T until it reaches the point b when it is run back into the flask. At the end of two hours the tube V is replaced by a longer one which reaches to K and distillation is continued until the ether reaches this point.

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The flask is now slipped off C, the bag is taken from the hook, and bag and flask are dried at the temperature of 220° F, until the weight is constant. The weight of the flask and contents minus the weight of the flask equals the weight of oil extracted.

The advantages claimed for this apparatus are its small cost, the fact that the substance treated is always subject to the action of boiling ether or its vapor, and that by means of the long siphon nearly all the ether is re-collected.

A. H. W.

INORGANIC ANALYSIS.

Estimation of Free, Half Combined and Combined Carbonic Acid in Mineral Water.—W. Borchers, Ztschr. anal. Chem. **26**, 720. When bicarbonates are present barium chloride should be added to the water before boiling. Barium carbonate is then formed and half of the carbonic acid set free. 1 to 1.5 gms. crystallized barium chloride per 300 c. c. water is sufficient in most cases.

Detection of Sodium Phosphate in Glacial Phosphoric Acid.—A. Bettendorff, Ztschr. anal. Chem. **27**, 24. The glacial phosphoric acid is dissolved in fuming hydrochloric acid and allowed to stand when common salt crystalizes out. 1 part of common salt dissolves in 1348 parts hydrochloric acid, sp. gr. 1.194 at 12°.

Estimation of Nitrites.—A. Vivier, C. R. **106**, 138. When an amide is treated with nitrous acid nitrogen is set free, and water and an acid corresponding to the amide are formed. In the case of urea we obtain carbonic acid. The author has applied this principle to the estimation of nitrites; the reaction is as follows: $CO(NH_2)_2+2HNO_2=CO_2+2N_2+3H_2O$.

The nitrogen obtained is, as will be noticed, twice the amount contained in the nitrite. The apparatus used consists of a flask to hold 150 c. c. provided with a stopper with three perforations. By one of these it is connected with an appa-

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ratus for furnishing pure CO_2, through the second passes a funnel tube with stop-cock, and the third is connected with an inverted Liebig's condenser, the other end of the condenser tube being connected with an apparatus for collecting the nitrogen such as that used by Duprè in his modification of Dumas' method.

The nitrite in solution is first passed into the flask, then urea in excess, and after the flask has been filled with CO_2 some sulphuric acid. The solution is boiled and the nitrogen collected over KOH and measured with the usual precautions. The method gives very exact results. Neither organic matter nor nitrates affect the results.

The Action of Sulphuretted Hydrogen on Arsenic Acid.—L. W. McCay, Chem. News, **57**, 54. The author, by adding to a solution of arsenic acid in sulphuric acid sulphuretted hydrogen water in quantity insufficient to precipitate the arsenic, has obtained a solution which acts as though sulphoxy arsenic acid, $H_3AsO_3S_2$, were present in solution. If this be true it solves the mystery which, since the time of Berzelius, has been connected with the action of sulphuretted hydrogen upon arsenic acid.

Estimation of Selenium in Meteoric Iron.—H. N. Warren, Chem. News, **57**, 16. 10 gms. of the iron in fine powder is mixed with sufficient sulphur in fine powder and introduced into a stout piece of combustion tubing. One end of the tube is connected with an oxygen gas-holder and the other end with a series of bulb tubes containing water. The selenium is burned to selenium dioxide and carried along by the sulphur dioxide into the bulb tubes, where it is reduced to selenium by the sulphurous acid. The water containing the selenium is heated to 80° F to make it denser and then introduced into a platinum dish, dried and weighed. A blank determination is made with the sulphur used. In 6 meteorites examined the selenium varied from 0.04 to 0.23 per cent.

No test analyses are given.

Determination of Lead in Tin Foil.—Y. Schwartz, Chem.

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Ztg. **12**, 52. 1 gm. of the alloy is warmed with 20 c. c. concentrated hydrochloric acid ; the action is usually at an end in half an hour when bromine water is added until the solution becomes yellow ; this dissolves all antimony. The solution is now boiled to drive off the excess of bromine, diluted to 100 c. c., allowed to cool, and poured in a thin stream into a solution of 40 gms. commercial, crystallized sodium sulphide in 150 c. c. water. After settling, the sulphide of lead is filtered, washed with dilute ammonium sulphide (1 volume ammonium sulphide from 10 per cent. ammonia and 9 volumes of water), dried and brought into a porcelain dish covered with a funnel. 10 c. c. nitric acid (1.5 sp. gr.) is added and then 5 c. c. concentrated sulphuric acid. The dish is warmed until the contents are colorless or have at most only a slight brown color. The solution is then allowed to cool, diluted with 50 per cent. alcohol to 100 c. c. filtered, washed with alcohol, dried, ignited and weighed. The weighed lead sulphate is dissolved in ammonium tartrate (100 gms. tartaric acid to 1 liter ammonia) and any remaining stannic oxide filtered off ignited and weighed and subtracted from the weight of lead sulphate found.

Separation of Stannic Oxide from Tungstic Oxide.—Donath and Müllner, Monatsh. Chem. **8**, 647. Bronzes containing tungsten and tin are now of more frequent occurrence than formerly and the need of an accurate and rapid process of separation has often been felt. The method is founded upon the fact that when a mixture of the two oxides is heated with very finely powdered metallic zinc the tin is reduced to the metallic state and becomes easily soluble in hot, dilute hydrochloric acid, while the tungsten is reduced to blue oxide, easily oxidized to tungstic oxide, insoluble in hydrochloric acid. The zinc used may be either zinc dust, zinc powder, or zinc filings. Zinc dust is most energetic but contains impurities, especially iron, lead and cadmium. Zinc filings should be made with a hard and very fine file and all particles of iron withdrawn with a magnet.

The heated and weighed mixture of the two oxides is rub-

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bed up with double the volume of zinc powder in an agate mortar, poured into a porcelain crucible and the mortar rinsed out with more zinc powder. The mixture is now heated strongly for 15 minutes in the covered crucible and after cooling boiled with dilute hydrochloric acid (1 acid to 2 of water) until all evolution of hydrogen ceases. The liquid is now cooled somewhat and pulverized potassium chlorate added cautiously until the blue tungstic oxide is completely oxidized to yellow tungstic acid. The liquid is now diluted with 1½ times its bulk of water and allowed to stand 24 hours. The tungstic acid is filtered off and washed, first with water acidified with nitric acid, and then with a dilute, hot solution of ammonium nitrate. The tungstic acid is then ignited and weighed. The stannic oxide is determined by difference, or precipitated as sulphide from the filtrate and converted into oxide by ignition in the air with addition of ammonium nitrate. The authors obtained the following results:

	Taken.	*Obtained.*
I	WO_3: 0.4654 SnO_2: 0.5041	WO_3: 0.4706
II	WO_3: 0.5943 SnO_2: 0.7003	WO_3: 0.5959
III	WO_3: 0.5622 SnO_2: 0.6475	WO_3: 0.5585
IV	WO_3: 0.0449 SnO_2: 1.1891	WO_3: 0.0431 SuO_2: 1.1912
V	WO_3: 0.8355 SnO_2: 0.0978	WO_3: 0.8307 SuO_2: 0.0970

In I and II zinc dust was used which contained lead and this accounts for the excess of WO_3 obtained. Generally a very small amount of WO_3 is lost. If the solution is allowed to stand 2 days before filtering the full amount is obtained.

The Estimation of Sulphuric Acid in Water Analysis.—O. Binder Ztschr. anal. Chem. **26**, 607. Wagner stated (Ibid. **20**, 321) that when water is evaporated over the gas lamp, sulphuric acid is taken up from the products of combustion. To test this the author evaporated distilled water, to which

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Na_2CO_3 had been added in amount equivalent to the lime found in natural waters, over the direct flame, an inverted funnel being suspended over the dish. Under these conditions sulphuric acid is taken up, in one experiment an amount equivalent to 0.042 gms. per liter. To avoid this source of error the water must, therefore, be evaporated over the water bath or on a large plate, so that the products of combustion do not reach it.

Indirect Estimation of the Alkalies, Especially in Presence of Lithium.—K. Kraut Ztschr. anal. Chem. **26**, 604. This method consists in heating the nitrates with silica and determining the composition from the loss in weight. The method may be used when the alkalies are present as chlorides, these being converted into nitrates by precipitation with silver nitrate, the excess of silver being removed by pure hydrocyanic acid. The method cannot be used when the alkalies are present as sulphates since, according to Diehl and Troost, barium sulphate always carries down lithia. The silica used is in the form of infusorial earth, and the method is especially useful in connection with Lawrence Smith's method for the estimation of alkalies in silicates.

Estimation of Antimony.—F. Muck, Ztschr. anal. Chem. **26**, 600. The precipitate of antimony sulphide mixed with sulphur, obtained in the usual way by solution in yellow ammonium sulphide and precipitation with acid, is filtered, washed and dried on the filter until the sulphide begins to separate from the filter in saucer-shaped pieces. These pieces are then removed to a glass plate as far as possible by means of a spatula. The funnel is then placed over an evaporating dish and the sulphide remaining on the filter dissolved by means of yellow ammonium sulphide containing a considerable excess of sulphur; very little need be used if it is run through the filter repeatedly. The solution is then poured, together with the ammoniacal washings into a crucible and evaporated over sulphuric acid (see page 176) and finally over the water-bath, adding the wash water from time to time. Instead of igniting in a stream of CO_2 it is better to convert the sulphide into

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Sb_2O_4. It is necessary first to separate the sulphur completely. This is done in the crucible by pouring in a few c. c. of carbon disulphide, and a larger amount of chloroform, covering with a watch-glass containing cold water, which is renewed from time to time, and heating on the water-bath for a few minutes. Any volatilized solvent condenses on the cold watch-glass and runs back into the crucible. The solution is now allowed to settle and the crucible placed in an evaporating dish and gently inclined until nearly all the solvent has run out. The outside of the crucible is rinsed off and the treatment with carbon disulphide repeated several times, until nearly all the sulphur has been extracted. Any pieces of sulphide left in suspension collect in the dish and are, after rinsing, returned to the crucible. The sulphide is then converted into Sb_2O_4 in the usual way.

The Detection of Nitric Acid in Well Water.—O. Binder, Ztschr. anal. Chem. **26**, 605. The method for detecting nitric acid by means of zinc, sulphuric acid, potassium iodide and starch is neither delicate nor certain, principally because an excess of zinc is employed which converts the nitrous acid formed into lower oxides of nitrogen. When pieces of zinc are used the amount of surface exposed is too small. The best way is to use a very small amount of zinc dust. Working in this way 20 mg. N_2O_5 per liter gives the reaction at once 2 mg. after 8 minutes and the N_2O_5 contained in distilled water could be detected after 12 minutes.

Hygienic Analysis of Air.—Klas Sondén Ztschr. anal. Chem. **26**, 592, describes an apparatus for this purpose, constructed upon the principle used by Otto Petterson (this Journal **I**, 216). For details the reader is referred to the original paper.

Etimation of Phosphoric Acid.—Isbert and Stutzer, Ztschr. anal. Chem. **26**, 583, have carefully examined the method which they proposed* for the estimation of phosphoric acid in fertilizers, Thomas Slag, etc. They find that the molybdate precipitate may be washed with water, instead of ammo-

*See also this Journal **1**, 349, 468.

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nium nitrate solution, without loss; and that when silica is present in solution the ammonium silicomolybdate which at first precipitates is washed out by the water; no mention is made of arsenic acid. Their experiments show that more than ½ liter of wash water may be used without loss of phosphoric acid. The analysis is conducted as follows: 5 gms. of the phosphate to be examined is dissolved in hydrochloric acid or aqua regia, diluted to ½ liter and filtered and 50 c. c. taken for analysis. Ammonia is added in excess to this and it is then acidified with nitric acid and the phosphoric acid precipitated with molybdic acid solution (at 60–70° the precipitation is complete in 15 minutes). The precipitate is allowed to settle and the solution to cool and washed with water by decantation until the wash water amounts to about 250 c. c. The precipitate together with the filter is now placed in an Erlenmeyer ¾ liter flask, excess of sodium hydroxide solution added and distilled into a measured volume of titrated sulphuric acid. The excess of acid is then determined with baryta water using rosolic acid as the indicator.

The following results were obtained:

	Gravimetric Method.	*Distillation Method.*
Phosphorite	25.70 per cent.	25.74 per cent.
Guano	21.41 "	21.45 "
Bone meal	25.10 "	24.03 "
Double superphosphate	42.60 "	42.66 "
Thomas phosphate	16.76 "	16.69 "
Bone meal	21.35 "	21.44 "
Phosphorite	23.76 "	23.74 "
Phosphorite	20.90 "	21.01 "
Guano	10.37 "	10.43 "
Ammonia superphosphate	9.22 "	9.24 "
Saltpeter "	10.88 "	11.01 "
Bone black superphosphate	17.15 "	17.13 "
Thomas phosphate	15.42 "	15.51 "

[One of the great objections to the direct gravimetric process, in which the molybdate precipitate is weighed directly,

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and to volumetric processes in which the amount of molybdic acid present is determined, is the danger of throwing down an excess of molybdic acid. It would seem, however, as if the ratio between the ammonia and phosphoric acid present should be a constant one. If the statements of Isbert and Stutzer should prove to be correct this process would, therefore, seem to be in the direction of greater accuracy. E. H.]

The Action of Sulphuretted Hydrogen upon Arsenic Acid.*—Brauner and Tomicek Monatsh. Chem. **8**, 607. By the action of a rapid current of sulphuretted hydrogen upon arsenic acid arsenic pentasulphide forms only slowly; the reaction is, however, complete if the solution is warmed and acidified with hydrochloric acid.

$$2H_3AsO_4+5H_2S=As_2S_5+8H_2O$$

In solutions of the pure acid, or with a slow current of gas in acid solutions the following reactions also occur.

$$H_3AsO_4+H_2S=H_3AsO_3+S+H_2O$$
$$2H_3AsO_3+3H_2S=As_2S_3+6H_2O$$

Volumetric Estimation of Boric and Phosphoric Acids.—C. Schwartz, Rep. anal. Chem. **7**, 700. When Congo red is added to a pyroborate and hydrochloric acid run in the color changes to blue when all the metal (sodium, in case of borax) has been converted into chloride and an excess of acid added. Insoluble borates are dissolved in an excess of acid and the excess determined; in this case the final color is orange. Addition of sodium chloride, potassium nitrate, magnesium sulphate, etc., has no influence upon the results. 1 c. c. $\frac{n}{10}$ $HCl=0.0044\ HBO_2$ and $0.002066\ H_3BO_3$.

Phosphates when titrated with hydrochloric acid change the color of Congo red to blue when they have been converted into monometallic phosphates (NaH_2PO_4).

The Analysis of Clay.—Meineke, Rep. anal. Chem. **7**, 757. The author finds that one statement made in his former paper upon this subject† is incorrect. It is there stated that the

*See also this Journal **1**, 405.
†This Journal **1**, 413.

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alumina when precipitated always contains silica which the evaporation to dryness had failed to separate, and that this must be determined and its amount added to that obtained by evaporation with acid. The author now finds that this silica comes from the ammonia employed, which always contains it when kept in glass vessels. The silica obtained from the alumina precipitate should, therefore, be subtracted from the alumina, but must not be added to the silica obtained by evaporation.

Apparaus for Volumetric Estimation of CO_2 in Carbonates.—D. Sidersky, Ztschr. anal. Chem. **26**, 336. This consists of, 1 a bottle for the decomposition of the carbonate with acid, the acid being placed in a rubber test-tube placed in an inclined position inside the bottle. The bottle is closed with a cork and connected by means of a rubber tube and glass tube passing through the cork and nearly to the bottom ; 2, an empty bottle, through the cork of which a thermometer passes ; this is connected by means of a rubber and glass tube with the upper end of 3, a graduated glass burette, open at the bottom and closed at the top with a cork. The stopper closing the upper end has two perforations. Through the second opening a short glass tube is passed and this is closed by a rubber tube and pinch-cock. The burette is placed in water contained in a large glass cylinder with tubulure at the bottom, closed with a perforated cork ; this is connected by means of rubber tubing with a bottle with doubly perforated cork, half-filled with water, which can be forced into the cylinder or drawn out by means of a rubber pressure ball, attached to the bottle by glass and rubber tube. The apparatus can be obtained from Paul Rosseau Cie Paris and is called by them "Calcimètre-Sidersky."

Estimation of Stannous Oxide.—G. Topf, Ztschr. anal. Chem. **26**, 285. When stannous oxide is titrated in alkaline solution (tartaric acid and sodium bicarbonate) with iodine solution and starch the results obtained vary and are very unsatisfactory ; this is also the case if the solution is first made acid. It is much better to add an excess of iodine to the hydro-

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chloric acid solution and to titrate back with thiosulphate. Even in this way satisfactory results are not obtained unless the mixture is digested for some time to secure complete oxidation. The best way is to bring the tin salt into solution with tartaric acid and bicarbonate, then to add an excess of iodine solution, acidify, and titrate back with thiosulphate.

IRON AND STEEL.

EDITED BY P. W. SHIMER.

Amorphous Silicon.—H. N. Warren, Chem. News, **57**, 54. For the preparation of amorphous silicon, commercial silicon eisen, cast into small bars, was suspended in a line connected to the positive wire of two ferric chloride cells, and immersed in sufficient dilute sulphuric acid for its complete solution, and in close contact with a large platinum plate connected to the negative wire. After the lapse of several hours the iron had completely dissolved, leaving a residue of graphite, together with silica and amorphous silicon.

Note on Chatard's Method for the Estimation of Small Quantities of Manganese.—T. E. Thorpe, F. R. S., and F. J. Hambly. J. Chem. Soc., March, 1888, p. 182. To the manganese solution, which must be free from chlorine and not too dilute, say about 25 c. c., add 5 c. c. concentrated nitric acid, 2–3 grms. of lead peroxide, and from 10–20 c. c. of dilute sulphuric acid (1 part of acid to 2 of water). Boil gently for about four minutes, wash down the sides of the flask with hot water, and continue the boiling for half a minute longer. Allow the lead sulphate and excess of peroxide to subside, and filter at once, by aid of a filter pump, through a plug of asbestus previously ignited and washed with dilute sulpuric acid. Wash the residue in the flask with boiling water by decantation, heat the clear filtrate to 60°, and titrate with ammonium oxalate.

The authors state that the method works well with weights of manganese from 0.004–0.008 grm., but is not to be de-

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pended on when more than 0.01 grm. is present. With 0.01 grm. in solution, the results were generally 0.0004 too low.

Solubility of Magnesium Ammonium Phosphate Alcohol.—Alfred J. Wakeman, Ph. B., Technology Quarterly 1, 173. Comparative experiments were made in the determination of phosphorus by washing one series of precipitates of magnesium-ammonium phosphate with a mixture of three parts by volume of water, and one part of ammonia (sp. gr. 0.96), and another series with the same ammonia water to which was added one part by volume of alcohol. With small precipitates the influence of the alcohol was not noticeable. With larger precipitates the use of alcohol in the wash-water showed a slight advantage, the magnesium-ammonium phosphate being slightly less soluble in this. The author finds, however, apart from the question of solubility, an advantage in the use of alcohol. The precipitate seems to be rendered more compact, is more easily washed, and is less liable to creep up the sides of the funnel. No advantage was found in adding alcohol to the solution in which the precipitation takes place. The precipitate, under these conditions, attaches itself closely to the beaker, and is not easy to remove.

Separation of Titanium from Iron.—Alex. Classen, Ber. d. chem. Ges., 1888, p. 370. For the determination of titanium in presence of iron, the author treats the hydrochloric acid solution of the substance with 50 c. c. hydrogen peroxide and 25 c. c. potassium hydrate solution, sp. gr. 1.30, and dilutes, according to the bulk of the precipitate, to 500 or 1000 c. c. and allows the oxide of iron to settle. An aliquot part of the clear solution is removed. This alkaline solution, which contains titanium trioxide and hydrogen peroxide, is heated in a covered beaker on the water-bath until the latter is decomposed, when a part of the TiO_3, mixed with TiO_2, is thrown down as a yellow precipitate. When the evolution of gas is ended, the solution is acidified with HCl or HNO_3, and heated until the yellowish-red colored solution is completely decolorized. The slightest possible excess of ammonia is added and

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the precipitate of titanic acid is filtered off, washed thoroughly with hot water, ignited and weighed.

ORGANIC ANALYSIS.

Detection of Acetic Acid in Presence of Morphine.—G. S. Johnson, Chem. News, **57**, 83. Ferric chloride solution added to morphine acetate gives first a blue color due to the morphine, which disappears on heating leaving the solution with the deep red tint of ferric acetate. The change in color takes place at about 80°.

The Estimation of Paraffin.—Zaloziecki, Ding. poly. Jour. **267**, 274. This method allows of the estimation of solid paraffin in lubricating oils, residues, vaseline, etc. It is founded upon the solubility of these mixtures in amyl alcohol from which the paraffin is precipitated on the addition of ethyl alcohol, the liquid hydrocarbons remaining in solution. 10–20 gms. of the substance is treated with five times the weight of amyl alcohol and the same amount of ethyl alcohol of 75° Tralles added. The mixture is allowed to stand for several hours at a temperature not exceeding 4°. The mixture is then filtered through a cold, dry filter and the residue on the filter washed with a cold mixture of 2 parts amyl and 1 part 70° ethyl alcohol. The residue is then placed in an extraction apparatus, the paraffin extracted with ether or benzene, the solvent evaporated for 2 hours at 125° and the residue weighed.

Becchi's Test for Cotton Seed Oil.—Ferdinand Jean, has made a trial of Becchi's test for cotton seed oil (this Journal, vol. 1, p. 449) and finds it reliable. He uses reagents of the following composition: 1st. A solution of 1 gm. silver nitrate in 200 c. c. of a mixture formed of equal parts of alcohol at 96° and ether. 2d. A solution of 85 parts of amyl alcohol and 15 parts of rape seed oil. The operation is conducted as indicated above except that the mixture is kept in the water-bath

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for 15 minutes. Even a brown coloration is said to be proof of the presence of cotton seed. (Journal de Pharm. et de Chim., Feb. 15. 1888, p. 199).

NOTE.—In all the English abstracts and in the one in this Journal already noted, the proportion of silver nitrate to be used is incorrectly given. Instead of one grain in 200 c. c. it should be one gramme as given above. When only one grain is used the reaction cannot be distinguished. H. W. W.

Reaction of Cotton Seed Oil with Lead Subacetate.—Take 5 c. c. of the oil in a test tube add a solution of subacetate of lead and then of ammonia and shake. A yellowish brown coloration is obtained characteristic of cotton seed oil. (Ibid p. 200.)

NOTE.—This reaction I have tried but without favorable results. I regard it as valueless for detecting the presence of cotton seed oil in mixtures. H. W. W.

Detection of Cotton Seed Oil in Olive Oil.—Milliau (Comptes Rendus 106 page, 530) calls attention to the reducing effect of free acids of cotton seed oil on silver nitrate. He uses the following method. 8 c. c. of the free acids are dissolved in 15 c. c. 90 per cent. alcohol and treated on the water bath for a few minutes with 2 c. c. of a solution of silver nitrate containing 30 g. in 1000 c. c. water. The characteristic phenomena of the Becchi test are produced.

(M. Milliau appears to be ignorant of the Becchi method of which his own is an unnecessary modification.) H. W. W.

Separation and Detection of Silk, Woolen and Cotton Fabrics.—Ztsch. Chem. Ind., Aug. 1887. Silk and cotton can be separated by dissolving the fiber in an ammoniacal solution of cuprous oxide and then adding a solution of sugar or gum, which precipitates the cotton, the silk being thrown down only when the liquid is acidulated.

An ammoniacal solution of oxide of nickel dissolves silk fiber only.

The invariable presence of sulphur in wool enables this fiber to be detected by means of a solution of alkaline plumbate.

Wool and silk are separated by treating the fiber with warm hydrochloric acid, which dissolves the silk very rapidly, while the wool is simply disintegrated.

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True silk is separated from "wild" silk by means of a saturated solution of chromic acid, diluted with its own volume of water. The mixed fiber is immersed in the liquid and the solution boiled for one minute. The true silk is dissolved completely, while the "wild" silk remains unaltered, even after two or three minutes ebullition. Wool comports itself towards this reagent in the same manner as true silk. "Wild" silk resists the action of alkalis much better than true silk.

Remout recommends the following modification of the method of Persoz for the separation of mixed fibers: The specimen is first boiled with water containing three per cent. of hydrochloric acid, by which any coloring matter, etc., is removed from the fiber. After being thus purified it is immersed in a boiling solution composed of:

Water	850 parts.
Zinc chloride	100 "
Zinc oxide	40 "

After washing and drying it is weighed and the loss of weight indicates the amount of silk contained in the specimen.

It is next heated to 100° with caustic soda solution of specific gravity 1.02 for about 15 minutes. The wool is dissolved, dried and weighed. Weight=amount of cotton in specimen. Loss of weight=amount of wool.

If a mixture of cotton, wool, true silk and "wild" silk is to be separated the specimen is treated with hot, concentrated hydrochloric acid. The true silk is dissolved in half a minute; the "wild" silk is dissolved at the end of two or three minutes' boiling. The remaining fiber is then treated with a solution of alkali, by which the wool is dissolved and the cotton left as a residue. I. A. P.

The Determination of Paratoluidine in Aniline Dyes.—C. Häussermann, Chem. Ztg., Oct., 1887. Recently there was published by P. Schoop a method for the estimation of paratoluidine in the anilines, based upon the separation of

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this amine in the state of the acetyl derivative. This method being condemned by the majority of the authorities, the author undertook to investigate the assertions of Schoop by following his method exactly in the estimation of paratoluidine in mixtures of known composition. With mixtures of pure aniline and paratoluidine and orthotoluidine containing less than .05 per cent. of paratoluidine, and operating under the most favorable conditions, the following results were obtained:

	Strength in Paratoluidine.	*Result of Analysis.*
Mixture No. 1	24.00 per cent.	19.34 per cent.
" " 2	6.00 "	0.00 "
" " 3	0.05 "	22.00 "

I. A. P.

Determination of the Reducing Sugars.—Robert Gedult, Mon. Scien., Jan. 1888. This method is based upon the estimation of the cuprous oxide resulting from the reduction of the Fehling's solution by means of an ammoniacal solution of silver chloride. The following equation expresses the reaction:

$$2AgCl+Cu_2O=Ag_2+CuO+CuCl_2$$

The determination is made either by collecting the metallic silver and weighing, or, as the author prefers, the amount of cupric chloride produced by the reaction is estimated by means of standard silver nitrate. As the oxidized sugars and some other organic substances that may be present tend to reduce the ammoniacal silver solution when either caustic potassa or soda is present these alkalies are removed by the addition of ammonium sulphate. It is necessary to keep the solution covered for the same reason. The oxidizing action of the air must also be carefully guarded against. Before the estimation of the cupric chloride the solution is feebly acidified with sulphuric acid. As potassium chromate cannot be used as an indicator on account of the blue color of the liquid and the large amount of ammonium sulphate present, the author makes use of a plate of polished copper upon which a drop of the solution is placed. When there is the slightest excess of silver nitrate

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present a grayish-blue stain of silver appears upon the copper. The author gives the following as some of the results obtained by his method :

Reagents used—

30 c. c. copper sulphate solution } According to Allihn.
30 c. c. tartrate solution }

Material, 25 c. c. of inverted sugar solution.

Silver reduced.	*Copper corresponding.*	*Inverted sugar according to Meissl's table.*	*Inverted sugar employed.*
Milligr.	*Milligr.*	*Milligr.*	*Milligr.*
253.4	149.1	0.0784	0.0788
491.1	288.9	0.1571	0.1576
459.0	270.0	0.1462	0.1470

For details of the operation and preparation of the reagents the original paper must be consulted. I. A. P.

The Detection of Hop Substitutes in Beer.—Chem. News. **57**, 53, 61.

Valuation of Indigo.—C. Rawson, Chem. News, **57**, 7, 19, 29, 34. A comparison of the different methods in use. The author also describes a new reduction process which depends upon the reduction of the indigotin to indigo white by means of sodium hyposulphite and lime, with subsequent oxidation of the solution by air, acidification with HCl to dissolve $CaCO_3$. The precipitate is dried and weighed and the indigo red extracted by means of alcohol. The author recapitulates as follows :

"1. Indigo when finely pulverized is completely dissolved by ordinary, concentrated sulphuric acid, at a temperature of 90° to 95° C, in the space of one hour.

"2. The permanganate method affords a quick and ready means for the approximate valuation of indigoes, but as substances soluble in dilute acids are, at the same time, more or less acted upon, the results obtained are somewhat too high.

"3. If the solution of indigo be saturated with sodium chloride, the coloring matter is thereby precipitated. When the precipitate is washed, dissolved in dilute sulphuric acid,

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and titrated with potassium permanganate, results are obtained which, for all practical purposes, are trustworthy and reliable. Indigo red and indigotin are simultaneously estimated by this modified process.

"4. Of all the volumetric methods which have been devised for estimating the indigotin, the sodium hyposulphite process is capable of giving at the same time the quickest and most accurate results; but, as has been previously stated, considerable care and delicacy are required in its manipulation. If the solution of indigo to be titrated with hyposulphite contain iron, in the ferric state, then the result obtained will be too high.

"5. Other bodies than indigotin, which are present in indigoes, are more or less affected by the process of sublimation, whilst indigotin itself is partly decomposed into a dark brown substance, which does not volatilize without complete destruction. According to the quality of the indigo, the results obtained by this process may be either too high or too low.

"6. The gravimetric reduction processes, as commonly described, are not quite so accurate as is generally supposed. Perfectly reliable and accurate results are, however, obtained by the use of sodium hyposulphite and lime water. The reduction is complete in less than half an hour. Where an exact chemical analysis is required, this method, I consider, gives the best results of any process which has hitherto been published."

Examination of Shoe Polish.—V. Hölbling, Ztschr. angew. Chem., 1888, **1**, 12. Shoe polish is manufactured by mixing oil of vitriol, molasses, bone-black, a fat, sometimes glycerine, and a tannate of iron obtained from green vitriol and galls. To this mixture soda or chalk is added to neutralize the excess of sulphuric acid. The analysis is conducted as follows:

A weighed portion is first extracted with boiling water and washed as long as the filtrate is colored. Filter and precipitate are now dried at 100° and weighed, brought into a

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Soxhlets extraction apparatus, extracted with light petroleum, and the fat dissolved weighed after distilling off the petroleum.

The residue, consisting only of inorganic material and carbon is now incinerated and the residue weighed. The difference in weight gives the carbon present. To determine the inorganic substances present, the ash from a separate sample is dissolved in concentrated HCl and the solution filtered from the slight insoluble residue. To the solution an excess of citric acid is added to prevent the precipitation of the calcium phosphate, ammonia is added to alkaline reaction and the lime precipitated with ammonium oxalate. In the filtrate from this the phosphoric acid is precipitated by magnesia mixture. The filtrate from the phosphoric acid is made up to 500 c. c. and 100 c. c. each taken for the estimation of sulphuric acid with barium chloride and of iron with nitroso-naphtol.* Soda is calculated by difference.

The fat obtained is examined by Koettstorfer's method and by Hubl's method in order to determine its character. The unsaponifiable oil is extrated from the saponified fat by means of light petroleum.

The aqueous solution obtained is diluted to 500 c. c. and the invert sugar in 25 c. c. determined. Glycerine is tested for qualitatively by the method of Reichl. 2 drops of the solution are mixed with 2 drops of melted phenol and an equal amount of sulphuric acid and the mixture heated to 120. If glycerine is present a brown solid mass is formed which dissolves in ammonia with a carmine red color. The quantitative estimation is made in 100 c. c. of the watery extract according to Becke.† The solution is saturated with elutriated barium carbonate to remove sulphuric acid, evaporated to a syrup, dried at 100°, weighed, incinerated, and the weight of the ash subtracted.

If more than 1 to 2 per cent. of iron is found in the ash, tannate of iron is probably contained in the polish. In this case a part of the watery extract is strongly acidified with

* See this Journal 1, 324.

† Ztschr. anal. Chem., 1880, 291

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hydrochloric acid, extracted with acetic ether and separated from the latter in a separatory funnel. The tannin is then brought into aqueous solution by adding water to the acetic ether and evaporating, and the solution is tested for tannin by ferrous sulphate and other reagents. If tannin is found it is separated as above from a definite portion of the watery extract and estimated by Lowenthal's method. The extractive substances are determined in the residue from the tannin extraction, by evaporation to dryness, weighing the residue, igniting to determine ash, and subtracting ash+sugar +glycerine from the total residue. The water in the polish is determined by drying it at 100°.

A polish examined by the author in this way gave :

Water	12.36	per cent.	Carbon	12.63	per cent.
Free sulphuric acid . .	1.38	"	CaO	16.06	"
Glycerine	3.45	"	SO_3	10.04	"
Invert sugar	10.49	"	P_2O_5	12.65	"
Extractive	5.37	"	Fe_2O_3	0.84	"
Mineral oil	4.02	"	Na_2O	5.78	"
Bone fat	4.89	"		99.96	"

The calculation from this was as follows :

12.65 parts P_2O_5 correspond to 27.62 parts $Ca_3(PO_4)_2$, or 32.87 parts bone-black (composition 84 per cent. $Ca_3(PO_4)_2$, 6 per cent. $CaCO_3$ and 10 per cent. C). This bone-black contains 10 per cent., or 3.28 parts carbon ; since 12.63 parts carbon are present, the polish contains 9.35 parts sugar carbon. This corresponds to 28.05 parts sugar. The sugar present in the polish is 10.49 parts, the total quantity of sugar added was, therefore, 38.54 parts. If the molasses used is supposed to contain 24.7 per cent. sugar, this corresponds to 156.03 parts molasses. The sulphuric acid necessary to carbonize the 28.05 parts sugar, reckoned on the basis of the reaction $C_6H_{12}O_6+2H_2SO_4=5C+CO_2+2SO_2+8H_2O$ is 30.54 parts+12.30 ($=10.04SO_3$)+1.38=44.22 parts. Finally the $5.78Na_2O=9.88$ parts soda. This gives, therefore, the following as the proportions to be used.

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	Calculated.	*In Round Numbers.*
Bone-black	32.87	33.
Molasses	156.03	156.
Sulphuric acid	44.22	44.
Soda	9.88	10.
Mineral oil	4.02	4.
Bone fat	4.89	5.
Glycerine	3.45	3.5

The author does not claim much accuracy for such a method of calculation, but thinks the results will sometimes prove of value.

Estimation of the Starch in Grain.—Dr. Monheim, Ztschr. angew. Chem. 1888, 1, 65. The author has compared the different methods for estimating starch and finds Lintner's method the best. The process of Asbòth* gives very irregular results. Lintners's process is as follows: 3 gms. of the pulverized grain is heated with 50 c. c. water in a pressure flask in a paraffin bath at 135–40° for 4 hours, then filtered and washed and after diluting to 200 c. c., poured into a flask with a cork and a long glass tube, 20 c. c. hydrochloric acid added and heated on the water-bath for 3 hours to convert the starch into sugar. The solution is then diluted to 500 c. c., the sugar determined with Fehling's solution and the number obtained multiplied by 0.916 to give the starch; 6 of such pressure flasks may be heated at once by means of a large paraffin bath provided with proper openings. The breaking of the covers, mentioned by Zipperer may be obviated if the flask is closed by a caoutchouc plate under which a piece of gutta percha is placed and upon these a lead plate of sufficient thickness, or a coin.

It is best to wash the contents of these flasks by decantation upon a filter of glass wool, using a filter pump toward the latter part of the filtration; in this way the filtration may be finished in 10 minutes. The addition of sugar of lead to bleach the solution, before adding Fehling's solution, as directed in some handbooks, is unnecessary and inadvisable;

*See this Journal 1, 348.

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the excess of lead must be removed by addition of 1 per cent. sulphuric acid or soda in such cases, and test analyses showed a decided difference in the amount of sugar found by this modification of the process.

Aldehydes in Alcohols.—Gayon (Bulletin de la Societe Chimique de Paris; 20 January, 1888, Vol. XLIX, No. 2, p 67), recommends the following methods for detecting and estimating aldehydes in alcohols. The reagent employed is prepared as follows:

$\frac{1}{1000}$ aqueous solution of fuchsine	1000 c. c.
30° B bisulphite of soda	20 c. c.
Pure concentrated HCl	10 c. c.

The bisulphite is poured into the fuchsine solution; after about an hour, when the decoloration is almost complete, the hydrochloric acid is added. The reagent is preserved in well stoppered flasks. Its sensibility increases for some days after its preparation.

The alcohol to be examined is reduced with pure water to 50 per cent. In a test tube mix 2 c. c. of the alcohol with 1 c. c. of the reagent. If the alcohol is free from aldehyde it will remain uncolored. If on the contrary it contains aldehydes the liquid is changed to a rose purple color, of an intensity proportionate to the quantity of aldehyde present.

The sensibility of the reagent is such that 1 c. c. of aldehyde can be detected in 500 liters of alcohol. H. W. W.

The Incineration of Organic Compounds.—H. Kronberg, Chem. Ztg. 11, 1600. The author describes an easier method than the one given by A. Köbrich.* For materials that swell up during incineration like sugar, or slightly detonate like the salts of the organic nitro acids, all that is necessary is a small platinum crucible and a good gas lamp. The material is weighed in a small test tube and dropped into the crucible a little at a time to avoid loss by swelling or spattering. When enough ash is obtained the test tube is again weighed. A thick platinum rod is used for stirring the contents of the crucible and projects through a notch in the lid.

*Chem. Ztg. 11, 1159. Jour. Anal. Chem. 1, 432.

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The covered crucible with its contents is heated to redness beginning at the side and going gradually toward the bottom.

The crucible is allowed to cool and more material is added from the test tube. The burning is repeated and this operation is continued as long as there is burning room in the crucible. The whole mass is then stirred up with the platinum wire and heated to a higher temperature. When nitric or sulphuric acids cannot be used to complete the incineration the crucible is cooled to the boiling point of water and boiling water is dropped in from the rim of the crucible by means of a glass rod until all the soluble salts are dissolved by stirring with the platinum wire, and the particles of carbon are collected on the sides of the crucible. The water is cautiously evaporated and the crucible heated to redness as before. This operation is repeated until the carbon is completely burned.

When incinerating the salt of the organic nitro acids the cover of the crucible is often covered with a coating of volatilized material which must also be incinerated. S. C.

Action of Bleaching Agents on Writing Ink.—R. Irvine, J. Soc. Chem. Ind. Dilute solutions act more slowly on ink the older the document. A very dilute solution of bleaching powder destroyed the color of newly written characters in 6 minutes, those 6 months old in 9–12 minutes, 2 years in 20 minutes; in a like time writing 6 years old was not greatly affected, 4 years very slightly, and 22 years hardly affected at all. Peroxide of hydrogen acts more slowly, but gives more definite results. The above statements apply only to ordinary gallotannate of iron ink.

Examination of Bone Fat.—E. Valenta, Zeit. Chem. Ind. 1887, **2**, 265. 1. *Determination of the Water.*—This is effected by drying a weighed quantity at 110°.

2. *Ash Determination.*—5–7 gms. of the fat are ignited in a platinum dish. The ash is weighed and 3, the amount of lime in it determined.

4. *Estimation of Total Fatty Acids.*—5–10 gms. of the fat is put in a small conical beaker, mixed with a corresponding

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amount of caustic soda solution (38° B) and twice as much alcohol and heated on the water-bath to saponification. The alcohol is evaporated off, water added and the soap decomposed with dilute sulphuric acid. The mixture is heated on the water-bath until the separation of the fatty acid is complete and a weighed amount (about 5 gms.) of stearic acid added. After the stearic acid has melted and become clear it is allowed to solidify. The solid cake is then lifted off, the acid replaced by clear water and the melting repeated. This melting with water is repeated several times and the fatty acid finally dried with filter paper, then at 110° and weighed. From the weight the amount of stearic acid added is subtracted; the remainder is the amount of fatty acid present.

5. *Estimation of the Free Acid.*—5–10 gms. fat are dissolved in absolute alcohol and titrated with $\frac{n}{5}$ potassium hydroxide with an alcoholic solution of phenolphtalein as indicator. The saponification number 205 may be used without sensible error.

6. *Estimation of the Saponification Number, the Iodine Number and the melting point of the Fatty Acids.*—The fatty acids are separated, by the method given above, from 10 gms. of the fat and the above determinations made in the ordinary way. Pohl's method is the best for the determination of the melting point.

Estimation of Ethyl Alcohol.—B. Röse, Ztschr. angewandt-Chem., 1888, p. 31. Two solutions are used. 1, a permanganate solution, containing about 10 gms. $KMnO_4$ per liter. 2, a $\frac{1}{10}$ normal solution of potassium tetroxalate. The author has estimated the alcohol in a 1 per cent. solution of the pure substance, only; and proceeds as follows: In a weighed 300 c. c. flask about 5 gms. of the 1 per cent. solution is poured and the flask again weighed. 50 c. c. of the permanganate solution is added and then 20 c. c. concentrated sulphuric acid. Under these conditions the alcohol is immediately oxidized to carbon dioxide and water. After standing for about a minute the solution is diluted with water. A measured volume in excess of the potassium tetroxalate solution is now added and the solution heated nearly to boiling

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and the excess of tetroxalate determined with potassium permanganate. The following results were obtained:

0.05002	gms. gave	0.05011	gms.
0.05011	"	0.05011	"
0.050042	"	0.05016	"
0.050020	"	0.05002	"

Examination of Cod Liver Oil for Vegetable Oils. — E. Salkowski, Ztschr. anal. Chem. **26**, 557. Different samples of cod liver oil show differences in melting point. All the samples tried became turbid after standing for 2½–3 hours at 10° to 12° and all the samples except 2 become solid; one sample solidified at 0°. When 20 per cent. of palm oil, cocoanut oil, or palm kernel oil is added and the mixture placed in melting snow the mixture solidifies in 30 minutes (cod liver oil of very low melting point was used). With 20 per cent. of linseed oil, cotton seed oil, and rubsen seed oil the mixture remains fluid. The determination of the solidifying point is, therefore, of use only in detecting adulteration with palm oil, cocoanut oil and palm kernel oil.

The Reichert-Meissel Method.—5 gms. of fat gave volatile acids sufficient to neutralize the following of $\frac{n}{10}$ caustic soda: Cod liver oil No. 1, 0.13 c. c.; No. 2, 0.10 c. c.; No. 3, 0.20 c. c.; linseed oil 0.94 c. c.; rubsen seed oil 0.48 c. c.; cotton seed oil 0.48 c. c.; palm oil 0.32 c. c.; cocoanut oil 7.28 c. c.; palm kernel oil 3.48 c. c.

The Sulphuric Acid Test.—When cod liver oil is dissolved in chloroform and some sulphuric acid added the mixture becomes violet blue, then purple, brownish-red, and deep brown. The author finds that this is due to the cholesterine contained in the fat; 100 gms. contain about 0.3 gm. Pure cholesterine does not give this reaction; but that separated from the fat, unless recrystallized from alcohol, contains a yellow coloring material, to which the blue coloration at first is due. The vegetable fats contain no cholesterine, but instead phytostearine. This crystalizes in tufted groups of solid and sometimes tolerably broad needles. Cholesterine crystallizes in very thin rhombic plates. Making use of this dif-

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ference it is possible to detect adulteration by separating the cholesterine and examining the crystals under the microscope. This separation is effected as follows: To 10 gms. oil in a flask 10 gms. KOH, an equal amount of water and 10 c. c. alcohol are added. The mixture is shaken and warmed slightly and saponification is completed in a few minutes. The solution is diluted with 600–700 c. c. water and shaken with 500 c. c. ether. After the ether has separated completely, which sometimes takes several hours (the separation may be hastened by addition of a small quantity of alcohol) it is separated, filtered through dry paper and distilled off until but a small amount is left. This is then warmed with some alcoholic potassa to saponify a little unaltered fat and again extracted with ether and the ether shaken with water to remove, as far as possible, any dissolved soap. The ether is evaporated and the residue dissolved in alcohol and allowed to crystallize, and the crystals examined with the microscope. The melting point of cholesterine being 146° that of phytostearine is 132–134 which is also an aid in deciding as to the purity of the oil under examination. Rubsen seed oil contains erucic acid and this separates from the ethereal solution in crystals which melt at 33–34°.

Amount of Free Fatty Acids—This determination is made by F. Hoffman's method (dissolving in ether-alcohol and titrating with alcoholic potassa and rosolic acid). The amount of free acid in good commercial cod liver oil does not exceed 0.69 per. cent., while in many vegetable fats it is greatly in excess of this amount: 0.29 per cent. for cotton seed oil, 0.75 in oil of almonds, 1.16 in olive oil, 1.66 in ground-nut oil, 2.29 in poppy oil, 2.96 in cocoanut oil, 3.45 in linseed oil, 4.28 in rubsen seed oil, and 13.26–13.39 in palm-kernel oil.

Detection of Sesame Oil in Cacaobutter.—Paul Zipperer, Chem. Ztg. **11**, 1600. 2 c. c. cacaobutter are gently warmed in a freshly prepared mixture of 1 c. c. HCl (1.18 sp. gr.) and 5 to 10 cg. cane sugar. If sesame oil is present a beautiful raspberry red color appears while pure cacaobutter thus treated is colored from a yellowish brown to a dark brown. S. C.

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Test for Aniline Colors in Red Wines, Fruit, Juices, etc.—C. O. Curtman Ztschr. anal. Chem. **26**, 555. 4 c. c. of the wine are mixed with 4 c. c. caustic potash solution and 2 drops of chloroform, and the mixture warmed gently for several minutes. If aniline colors are present phenyl isocyanide is formed and recognized by its penetrating odor. Rosaniline, sulpho rosaniline, aniline blue, aniline purple, aniline violet, magenta, ponceau red, and several yellow and green so-called "aniline colors" can be detected in this way.

Examination of Indigo Colors.—W. Lenz, Ztschr. anal. Chem. **26**, 535. This article contains a formidable array of tables for which space fails us, and we must therefore refer the reader to the original.

Detection of Alcohol in Chloroform.—Ad. Jolles, Rep. anal. Chem. **7**, 425. When a fragment of potassium manganate (vol. 1 p. 400 of this Journal), is placed in contact with chloroform which contains alcohol, yellowish brown flakes are formed at the points of contact, on standing. The intensity of the reaction and the extent to which it takes place is in direct proportion to the amount of alcohol present. This subject is further discussed by Jolles in the Chemiker Zeitung **11**, 1394.

Nitrogen Determination by Kjeldahl's Method.—L. Lenz, Ztschr. anal. Chem. **26**, 590. The author has made comparative determinations of the nitrogen in albumen, skin, ivory, bone meal, etc., in one series of determinations using potassium permanganate to complete the oxidation and in a second series without the permanganate. He finds that slightly higher results are always obtained when permanganate is used.

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ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

Oxygen.—An important determination of the atomic weight of oxygen has been made by Cooke and Richards, (Proc. Amer. Acad., v. 23, p. 149). Hydrogen, purified with extraordinary care, was weighed in large glass globes, and then burned. The water formed was also weighed, and the oxygen taken by difference. The experiments are divided into three series; first, with hydrogen evolved from zinc and sulphuric acid; second, with hydrogen obtained by electrolysis; and third, with hydrogen developed by the action of potassium hydrate upon aluminum foil. In this way errors due to possible impurity in hydrogen derived from only one source were sought to be avoided.

SERIES I.

Weight of H.	*Weight of H_2O.*	*At. Wt. of O.*
0.4233	3.8048	15.977
.4136	3.7094	15.937
.4213	3.7834	15.960
.4163	3.7345	15.941
.4131	3.7085	15.954
	Mean,	15.954 ± .0048

SERIES II.

.4112	3.6930	15.962
.4089	3.6709	15.955
.4261	3.8253	15.955
.4197	3.7651	15.942
.4144	3.7197	15.953
	Mean,	15.953 ± .0022

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SERIES III.

.42205	3.7865	15.943
.4284	3.8436	15.944
.4205	3.7776	15.967
.43205	3.8748	15.937
.4153	3.7281	15.954
.4167	3.7435	15.967
	Mean,	15.952 ± .0035

Total average, O=15.953±.0017.

In the hydrogen used for the determinations the only possible impurity was nitrogen. That element was looked for spectroscopically, but none of its lines could be found. It is, however, by no means certain that minute traces of N could be detected, and that point, therefore, remains to be cleared up. The effect of nitrogen in the hydrogen as weighed would be to lower the apparent atomic weight of hydrogen; and would therefore exert an adverse influence in the discussion of Prout's law.

Morley (Am. Chem. J. **10**, 21) discusses Scott's work on the composition of water, and gives an outline of proposed methods for determining the atomic weight of oxygen.

Lord Rayleigh (Chem. News, **57**, 73) has redetermined the density ratio between H and O, and finds it to be 1:15.884. The application of this to ascertaining the relative atomic weight of the two elements depends upon our knowledge of the composition of water by volume. The latter question is being further investigated by Scott.

Copper.—Richards (Proc. Amer. Acad. **22**, 346) determines the atomic weight of this element by the precipitation of silver from a solution of pure silver nitrate by pure metallic copper. In six experiments, if Ag=107.675, the value of Cu=63.437. The precipitation was effected in ice cold solutions, and the silver was dried at 150°.

In a second paper (Proc. Amer. Acad. **23**, 177) Richards finds that the silver of his former weighings contained still a

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trace of moisture. Five additional experiments were, therefore made, in which the silver before weighing was heated to incipient redness.

Weight Cu.	*Weight Ag.*	*At. Wt. Cu.*
.75760	2.5713	63.450
.95040	3.2256	63.451
.75993	2.5794	63.447
1.02060	3.4640	63.448
.90460	3.0701	63.452
	Mean,	63.450, ±.0006.

Gold.—A further criticism of Thorpe and Laurie's work is published by Krüss. (Ber. **21**, 128).

Iron, Zinc, and Aluminum.—Torrey (Am. Chem. J. **10**, 73) publishes determinations of the equivalents of these metals made by students in his laboratory. In each case the hydrogen evolved by a solution of the metal in acid (generally hydrochloric acid) was measured. The paper is chiefly interesting from the stand-point of the teacher, as showing how closely students can be trained in the determination of such constants. The results are crude, but approximate very closely to recognized values.

AGRICULTURAL ANALYSIS.

EDITED BY H. W. WILEY.

Water in Superphosphates.—At the November meeting of the Society of Chemical Industry, a discussion took place on Mr. Ruffles' paper on "Analyses of Superphosphates" printed in the July number of the Society's Journal. (See this Journal, vol. 1, p. 455.)

Mr. Newlands said that Mr. Ruffle attached too much importance to the quantity of water. His process would give the percentage of uncombined water, but this percentage would vary from week to week. In a manure exported to

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America the moisture determined by the $CaCl_2$ method might be 10 per cent. On its arrival in America, some weeks later, the results would appear so much lower that the American buyer would be apt to lose faith in the skill of the London analyst.

Mr. Hughes said the difficulties which arose between the manufacturers of superphosphates and American buyers practically turned on the question of what *was* water. If manufacturers would adopt either the $CaCl_2$ method or the water-bath method, all dispute might be avoided.

Mr. Crowder said if a superphosphate contained free acid it was clear that it was badly made. The whole of the P_2O_5 was calculated as monocalcic phosphate whereas really only two-thirds of it were in this condition.

Mr. Ruffle in reply said it was true the results of his method would vary with time but the manure itself varied.

The sulphate of lime could not be determined from the lime in each case. This might be possible in ammoniated superphosphates owing to their containing practically no lime as monocalcic phosphate, yet in plain superphosphates the amount of lime present as monocalcic being appreciable, was yet too irregular to permit any rule. He did not believe American buyers would succeed in forcing manufacturers to guarantee a certain condition on arrival. No maker would agree to that, not knowing the time which would be taken in transit. (Journal Society Chemical Industry, Vol. VI, No. 11, pp. 704, *et seq.*).

Determination of Potash.—Lindo has examined Gladding's method of estimating potash as recommended by the Association of Official Agricultural Chemists, at the second annual meeting, 1885.

He applied the method to the determination of potash in manures of known composition. The results were most satisfactory.

In five samples taken from the same package of the fertilizer the per cents. of K_2O found were 7.24; 7.25; 7.05; 7.12 and 7.11, respectively.

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In another series of experiments the per cents. obtained were, 6.96; 7.03; 7.00; 7.00; 6.97, and 6.99, respectively. In these cases the manure had absorbed a little moisture which lowered the per cents. of all the constituents in the same ratio as shown in the potash results.

The method uniformly gives results a little below the actual quantities of potash present. With manures containing less than 8 per cent. K_2O this error will not be greater than .1 per cent. In closing Mr. Lindo says:

"I may conclude by observing that the difficulty in arriving at perfectly concordant and accurate results in estimating the various constituents in these manures is often considerable, owing to their hygroscopic instability and the great trouble which getting a uniform mixture entails.

"The method proposed by Mr. Gladding is simple and expeditious and in these respects much superior to the standard method, which, if we are to judge by the published figures, does not often give as accurate results, even in the hands of experienced analysts, as the method of Gladding." (Chemical News, Vol. 56, pp. 163, et seq.).

NOTE.—The method of Lindo and Gladding adopted at the meeting of the Association of Official Agricultural Chemists, is published in Bulletin No. 16, Division of Chemistry, U. S. Department of Agriculture, pp. 60–61. This bulletin is now entirely out of print. The method has also been detailed in this Journal, Vol. 2, p. 12.

Estimating Volatile Acids in Butter.—Dr. Rudolf Wollny, has made an exhaustive study of the sources of error in the Reichert-Meissl method of estimating the volatile acids in butter fat. His studies have led him to the following conclusions:

1. The error due to CO_2 absorbed during saponification may amount to plus 10 per cent.

2. The error due to formation of butyric ether may amount to minus 8 per cent.

3. The error due to formation of ether during distillation may amount to minus 5 per cent.

4. The error due to cohesion of fatty acids during distillation may amount to minus 30 per cent.

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5. The error due to shape and size of vessel in which the distillation is performed and to the speed of distillation may amount to plus or minus 5 per cent.

The best method to avoid these losses is, according to Wollny, the following :

Five grammes of the clear butter fat are accurately weighed into a 300 c. c. flask, round form ; length of neck 7 or 8 cm., width of neck 2 cm. ; two c. c. 50 per cent soda solution which must be preserved so that carbonic acid cannot be absorbed, and 10 c. c. 96 per cent alcohol are added and the mixture is heated under a reflux condenser for 15 minutes in a boiling water bath. The alcohol is then distilled off whilst the flask is heated for at least half an hour ; 100 c. c. boiling water are added under due precautions and the flask heated until the soap is completely dissolved. 40 c. c. H_2SO_4 (25 c.c. H_2SO_4 in 1000 c. c.) and two pieces of pumice the size of a pea are added and the flask is at once connected with a condenser by means of a glass tube 7 cm. wide, and having at a distance of 1 cm. above the cork, a bulb of the diameter of 2.5 cm. The tube is bent immediately above the bulb upward in an oblique angle, in which direction it extends 5 cm., and is then bent downwards in an oblique angle, and connected with the condenser.

The flask is then heated with a very small flame until the insoluble fatty acids are completely fused.

110 c. c. are then distilled off, the time required being 30 minutes. The distillate is mixed and 100 filtered off, 1 c. c. phenol-phtalein is added and titrated with deci-normal baryta solution. Add one-tenth to the number obtained and deduct the amount of the blank determinations which should not amount to more than .33 c. c. (Analyst, Vol. 13, No. 142, February 1888, p. 40.)

Effect of Storage on Superphosphates.—The comparative merits of the Petermann * and Wagner † methods of estimating phosphoric acid are discussed. The only variations from

* Bulletin de la Station Agricole à Gembloux No. 33.

† Fresenius Quantitative Analysis 2, 6th German edition, 703.

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the described methods was in using preliminary precipitations with molybdic acid in the presence of large quantities of iron and alumina.

The following conclusions were deduced from the results of analysis:

1. The Petermann method used with superphosphates gives higher results under the circumstances than Wagner's.

2. With superphosphates poor in oxide of iron and alumina the difference between the two methods, within a short time of dissolving, is not so great, but in eight days the phosphoric acid found by the Wagner method goes back to such an extent that of 100 parts previously soluble 17 parts become insoluble.

3. With superphosphates rich in ferric and aluminic oxides considerable differences exist at first between the results of the two methods and on storing these differences always increase.

(A. Beyer in Chemical News, Vol. 57, p. 63, translated from Repertorium der analytische Chemie, Vol. VII, p. 22).

Foreign Oils in Butter.—T. T. P. B. Warren proposes chloride of sulphur to detect vegetable oils in butter. The butter is filtered through asbestos by means of CS_2. After driving off the solvent the weight of fat is determined.

The fat is then again dissolved in CS_2 and an equal volume of yellow chloride of sulphur added, previously diluted with an equal volume of carbon disulphide. The CS_2 is then completely dissipated on the water-bath. In case of a pure butter the resulting mass will yield a clear solution with CS_2. An insoluble residue will indicate the presence of a vegetable oil. Animal fats in general behave like butter.

When the yellow chloride of sulphur is added to oils a very violent action takes place—hence the necessity of mixing the chloride with some suitable solvent.

The action of castor oil is so violent that a larger quantity of dilutent must be used than for other oils.

The possibility of estimating the quantity of added vegetable oil is set forth, since it is claimed these oils remain insol-

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uble in bisulphide of carbon after the treatment described.

Cocoa nut oil behaves unlike other vegetable oils, and more like butter when treated with sulphur chloride. The product formed however is much darker than with butter.

In a qualitative experiment there was taken of—

Oleomargarine	5.76	grams.
Cotton seed oil added	5.24	"
Residue after treatment with sulphur chloride, etc.	7.74	"
Due to cotton seed oil added	5.67	"
Increase due to cotton seed in oleomargarine . .	2.07	"
Hence cotton seed originally present in oleomarg'e	33.3	per cent

Two experiments with cotton seed alone gave results within 5 per cent. of each other.

"A fact which adds importance to this method of testing is that if cotton seed oil be added to oleomargarine or pure butter, the well-washed solid product obtained is colored by a portion of the animal fats, which is so far pronounced that no difficulty can arise in deciding whether the animal fats are those belonging to pure butter, or whether they belong to certain soft fats or oleines." (Chemical News, Vol. **56**, 222, 243 and 262.)

Potash in Soil and Plants.—Berthelot and Andrè show that potash cannot be accurately determined in a soil unless the silica be previously destroyed with fluohydrate of ammonia. In a vegetable mould they found for each kilogramme of the dry earth 8.92 g. of potash.

50 Kg. of the same earth lixiviated with 50 kg. of pure water added in successive portions gave for each kg. earth 0.0029 g. K_2O.

200 g. of the same earth rubbed up with a liter of cold distilled water allowed to stand 24 hours and then filtered gave per each Kg. 0.0305 g. K_2O.

Further experiments made with pure water led to the conclusion that an indefinite amount of water acting for a short time would remove about one-fortieth of the total potash in the soil.

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Previous calcination of the earth does not increase the quantity of potash removed by pure water.

When 8 g. sugar was added to 400 g. water the quantity of potash dissolved was increased three fold. This seems to show that sugar has a specific action in rendering potash soluble by diminishing the absorbent power of the soil, or perhaps more exactly by dissociating the compounds which retain the potash in an insoluble state. Acetic ether and ammonia do not increase the solvent action of water; whereas acetamide and carbonic acid do.

Hydrochloric acid dissolves about 100 times more potash than water and a third more than nitric or acetic acids. These acids, hot, remove a considerably larger proportion of potash.

To obtain useful results it is necessary to estimate all the potash in the soil and as has been said, this can only be accomplished after the removal of the silica. No sharp line of demarcation exists between the potash of a soil immediately assimilable and that capable of becoming so during annual vegetation.

It does not suffice in this regard to estimate the potash extracted by treating the soil with pure cold water, or by a very weak cold acid. Not only is this method very imperfect, the quantity soluble varying with the temperature and the conditions of the experiment, but this quantity is also so small a fraction of the total as to afford no serious information concerning the reserves of this alkali remaining in the soil nor of the proportions of complementary potassic fertilizers which would be required.

For the study of potash in the vegetable tissues the plant *Mercurialis Annua* was selected.

The whole plant, carefully dried at 100° gave 1.25 per cent. ash, chiefly composed of the salts of lime and potash.

The ash contained of K_2O 23.30 per cent.

A portion of the dry pulverized plant was treated with ten times its weight of cold distilled water for 24 hours.

The filtered liquor was evaporated to dryness, the residue

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incinerated and examined for potash. The quantity obtained was 18.92 g. for 1 kg. of the dried plant, about two-thirds of the total potash in the plant.

With dilute HCl 24.58 g. per kg. was obtained.

The potash in a plant may therefore be divided into three parts :

1st. That which is easily soluble in water.

2d. That difficultly soluble in water and soluble in dilute acids.

3d. That retained by the tissues of the plant against the solvent action of water and dilute acids.

Examination of decaying vegetable matter led in general to the same results, viz : that by water and weak acids alone only a part of the potash could be obtained. Even after the incineration of this mold only the half of the potash could be obtained.

These experiments may throw some light on the function of decaying vegetable matter in the soil. It certainly does not retain all of the potash originally in the plants, a portion having been removed by the action of the rain.

It (vegetable mold) is a true complementary fertilizer, of rapid action, intermediate between mineral manures on the one hand and organic fertilizers on the other. (Comptes rendus, **105**, 833 and 911).

Sulphur and Phosphorus in Soil and Plants.—Berthelot and Andrè have made studies of sulphur and phosphorus in soil and plants similar to those of potash.

To determine sulphur in agricultural products it is necessary to determine :

1st. Sulphur existing as sulphates directly precipitable as sulphate of barium.

2d. Sulphur in the form of compound ethers, similar to ethyl sulphates and glycerisulphates decomposable by hydratation under the prolonged influence of acids or weak alkalies.

3d. Sulphur in the form of mineral compounds, such as sulphides, sulphites, hyposulphites and other salts of sulphur acids, transformable into sulphates by wet methods and by the

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continued and energetic action of oxidants like nitric acid.

4th. Sulphur in the form of organic compounds, such as taurin, cystin, albumin, etc., compounds in which the sulphur is not completely converted into sulphates in the wet way, at least not in ordinary conditions.

The following method was employed to determine the total sulphur in plants and humus soils.

The sample previously dried at 100° is burned in a current of oxygen and the resulting vapors passed through a long column of pure anhydrous carbonate of potash or soda.

This operation is carried on in a tube of hard glass at a temperature near redness but not high enough to fuse the alkaline carbonates. When the organic bodies are completely incinerated the current of oxygen is continued for some time, keeping the temperature near redness, in order to transform all the sulphur compounds into sulphates. After dissolving the residual mass in water and acidulating with hydrochloric acid, the sulphates are precipitated with barium chloride.

The phosphorus can be determined in the filtrate after the separation of the barium salts, or on a separate sample of the material in the presence of the sulphuric acid.

From a soil the quantities of sulphur obtained by treatment

with dilute HCl cold was	per Kg.	0.182 g.
By boiling HNO_3 for 1.5 hours	"	0.212 g.
By combustion in oxygen	"	1.418 g.

In vegetable mold the following numbers were obtained :

Cold HCl	per Kg.	0.947 g.
Boiling HNO_3	"	2.021 g.
Combustion in oxygen	"	6.156 g.

In dried *Mercuriatis annua* :

HCl cold	per Kg.	2.834 g.
HNO_3 boiling	"	4.554 g.
Combustion in oxygen	"	6.584 g.

Phosphorus.—Phosphorus may exist in plants—

1st. In the form of phosphates, soluble or insoluble in water but soluble in mineral acids.

2d. In the form of compound ethers, like phosphoglycerates

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and glucophosphoric acid, decomposable by hydration and affording phosphoric acid under the influence of oxidants.

3d. In mineral compounds, as phosphides, phosphites, etc., transformable into phosphates in the wet way and by oxidants.

4th. In the form of organic compounds, like oxide of triethyl phosphine, phenylphosphorated compounds. cerebric acid, etc. ; bodies very difficultly transformable by oxidants into phosphoric acid, by the wet method.

The analytical results, like those with sulphur, show that only by combustion in oxygen can the total phosphorus be determined.

It is seen by these experiments that sulphur and phosphorus as well as nitrogen, exist in the soil, in vegetable mold and in plants under multiple forms ; that these elements can only be determined in totality by a total destruction of the organic matter at a red heat and that all loss by volatilization is avoided by the processes described. (Comptes rendus, **105**, 1217.)

Phosphorus and Phosphoric Acid in Vegetation.—In continuation of their studies on phosphorus in plants, Berthelot and Andre (Comptes Rendus, Vol. 106, pp. 711 and following) give the results of their latest investigations. The plants selected were Amarantus Caudatas and Amarantus Pyramidalis. It is shown that at the commencement of growth the plant began to abstract phosphorus from the soil and that this element increases in absolute proportion until the flowering of the plant. At this time the fixation of the phosphorus is arrested although the plant continues to increase in absolute weight. The relative weights of phosphorus, potash, and nitrogen are as follows :

	P. per cent.	*K_2O per cent.*	*N. per cent.*
31st May	1.7	3.2	2.3
5th July	.73	2.	2.3
2d August (in flower) .	.67	4.	2.2
30th September . . .	.33	3.	1.2

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In the second experiment the pot in which the plants were grown contained 45.5 kg. of dry earth, 7.8 kg. of water. The soil had at first been exhausted of nitrates by lixiviation. It was supplied with seven to eight liters of water during the growth of the plant. The phosphorus, the nitrogen and the potash were in the same proportion as in the preceeding experiment. The relative per cent. of these different substances in the plant at different times were as follows :

	P. per cent.	*K_2O per cent.*	*N. per cent.*
31st May	1.74	3.2	2.3
5th July	1.77	2.75	2.
2d August (in flower) .	.88	3.66	2.2
20th September . . .	.61	2.76	1.

The following experiment is still more striking, in which acetate of potassium was added in considerable proportion to the soil in the experimental pots.

	P. per cent.	*K_2O per cent.*
31st May	2.	6.74
15th July	.40	6.10
22d August	.70	7.49
20th September (in flower)	.34	6.22

The authors say : "Although the plant was charged with potash in a proportion more than double that developed in ordinary soil it did not take any more phosphorous than usual; the relative proportion of this element being almost the same as in the first experiment at corresponding periods of vegetation."

"It likewise remained almost stationary after flowering. We propose to find out during the next season to what point these results can be made general and extended to other species."

Sources of Nitrogen in Vegetation.—Gilbert and Lawes have reviewed the whole subject in the light of the long continued experiments at Rothampstead. The gain and loss of the soil in nitrogen is discussed and the action of nitrifying organisms set forth.

They find in the soil at Rothampstead a quantity of combined nitrogen equivalent to 2200 tons per hectare.

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This they think is about the mean quantity in cultivated soils. They point out the course of experiments which may lead to a satisfactory explanation of the manner in which these stores of nitrogen may be made available. The discussion is too long to give even in condensed form. (See original articles in Proceedings of Royal Society 1887, and Annales Agronomique, Vol. 14, No. 2, pp 78 et seq.)

Nitrogenous Salts in Plants.—Herbaceous plants contain in general more nitrites than the ligneous. Nitrites, although abundant in the soil, have never been discovered in the plant. The nitrites reported in plants, in botanical literature, are only errors of observation or of erroneous interpretation. The plant has the power of reducing any nitrite absorbed with wonderful rapidity, and that is the reason they are not found. Nitrates on the other hand can remain in the plant for weeks and even months without being destroyed.

Nitrites even in dilute solution have a deleterious effect on vegetation. Plants which receive their nitrogen in the form of nitrite of ammonia never contain nitrates. Neither nitrous acid nor ammonia is oxidized in the plant to nitric acid, (Molisch, in Journal de Pharm. et de Chèm. 15 Feb., 1888. Abstract from Sitzungsberichte der Akad. der Wissenschaft in Wien., 1887).

Estimation of Ammonia in the Soil by the Azotometric Method.—Baumann (this Journal, Vol. I, pp. 232 et seq.) discussed the various methods in common use for the estimation of ammonia in soils.

Knop (Ztschr. anal. Chem. **26**, pp (et seq.) proposed certain modifications of the methods there described and attributed to him. These changes are as follows:

1. In the new method it is not stated that the borax solution is to neutralize the free alkali of the bromine solution.

2. The contraction of the sample of earth with the concentrated borax solution is carefully measured beforehand, by carefully adding soda-lye, until the contraction begins, and then using a less quantity than this in the final estimation of the ammonia.

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3. Not more than 100 g. of soil should be used.

4. The shaking during the driving off of the ammonia should not be carried to excess.

Baumann (Ztschr. anal. Chem. **26**, pp. 302 et seq.) points out the errors in the old methods and subjects Knop's proposed changes to a rigid criticism. The error due to loss of nitrogen caused by the action of bromine on soils rich in humus, does not seem to be taken into consideration by Knop.

Volumetric Determination of Soluble Phosphoric Acid in Superphosphates.—The solution of superphosphates mixed with $CaCl_2$ is allowed to flow into a standardized solution of soda lye, to which some phenol phthalein has been added.

The following reagents are required:

1. A soda lye of which 1 c. c. represents about .005 P_2O_5.

2. Calcium Chloride solution made by dissolving 200 g. $CaCl_2$ in one liter of water.

3. Phenol-phthalein, 1 g, in 500 c. c. alcohol.

4. Methyl orange in aqueous solution.

The execution of an analysis is carried on as follows:

200 c. c. of the solution of the sample prepared in the ordinary manner are mixed with 50 c. c. solution of calcium chloride and well shaken. One burette is filled with this mixed solution and a second with soda lye. Of this latter 20, 10, or 5 c. c. (according to the strength of the superphosphate) are measured into a beaker; 2 c. c. of the phenol-phthalein solution are added and some water, and superphosphate solution is then run in rather rapidly. As soon as the color begins to grow faint the superphosphate liquor is added more gradually, and at last drop by drop, until the redness has entirely disappeared. The recognition of the concluding point, however, requires some experience. As it is necessary to use a large quantity of the indicator the change of color is not instantaneous, and the reaction is not complete until the last trace of a reddish tone has entirely disappeared, and there appears in its stead a whitish, faintly brown, or yellowish coloration. A re-appearance of redness need not be regarded unless it ensues very quickly and decidedly. Frothing ren-

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ders the recognition of the change more difficult, whence it should be avoided as far as possible. The determination should then be repeated, advancing more rapidly towards the point of saturation.

The author next measures off again the same number of c. c. of the mixed solution of superphosphate and calcium chloride as used above, dilutes with a little water and mixes with 4 to 6 drops of the methyl-orange solution, so that a distinct violet-red colour is produced by the free acid. The liquid is titrated cautiously with the soda-lye, finally drop by drop until the reddish colour changes to a yellow or orange yellow. Here also the recognition of the final point requires a little practice ; the change is more distinct if the liquid has a moderate coloration. After this experiment also has been repeated the smaller number of c. c. of soda-lye, as consumed in the titration with methyl-orange, is deducted from the number obtained on titrating with phenol-phthalein. Thus is obtained the quantity of soda lye requisite for precipitating the phosphoric acid as tricalcium phosphate. If we have dissolved 20 grms. superphosphate in 1000 c. c. of water and made up to 200 to 250 c. c. by the addition of 50 c. c. of the calcium chloride solution, and if *a* is the measured quantity of soda-lye, *b* the solution of superphosphate and calcium chloride consumed, *c* the soda-lye used for neutralizing the free acid, and *t* the standard of the soda-lye expressed as P_2O_5, the percentage of soluble phosphoric acid in the sample is *equal to* $(a-c) \times t \times \frac{250 \times 1000 \times 100}{200 \times b20}$

This method is applicable to ferruginous superphosphates.

(A. Emmerling Ztschr. anal. Chem. **26**, p 244. Abstracted in Chem. News, Vol. **57**, p. 15.)

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TOXICOLOGY.

EDITED BY V. C. VAUGHAN.

Alkaloidal Bases in Alcohols.—Hygienists have been occupied for some time in examining alcohols for organic bases to which toxic properties were ascribed.

Lindet, (Comptes rendus, Vol. 106, pp. 280, *et seq.*) has undertaken to determine the quantity of such bases in alcohols by the moist combustion process of Kjeldahl.

From .5 to 1 liter of the alcohol is reduced with water to 50 per cent strength (50° Gay Lussac), with the addition of 20 g. H_2SO_4. It is then shaken for some time and slowly distilled until all the alcohol and all the water are driven off. The sulphuric acid at first blackens the residual organic matter, then burns it with the evolution of SO_2 and finally becomes clear.

Half a gramme of mercury is then added and the heat continued half an hour longer and kept just below the boiling point of the liquid. The liquid is diluted with water, transferred to the distillation apparatus and the ammonia driven off after the addition of sulphide and of caustic potash.

The process is very sensitive, permitting the estimation of one millionth part of base. The amount of base is found by multiplying the ammonia by 4.25.

In alcohols made from cereals very little base was found, varying from 3.65 to 1.76 mg. per liter. On the other hand the products of fermentation of beet molasses were rich in base, in one instance as high as 97.96 mg. per liter.

The small quantity of base in the products of cereal fermentation is ascribed to the fact that when the starch is saccharified by acids a temperature of 120°–130° is employed, and if by malt 65°–70°. At these temperatures the activity of the germs to which the genesis of the organic bases is attributed is destroyed in the one case and greatly diminished in the other.

H. W. W.

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Composition of the Organic Bases in Alcohols.—Respecting the organic bases found in alcohols, Morin (Comtes rendus, Vol. 106, pp. 360 *et seq.*) has made the following observations. By fractional distillation three bases were isolated.

No. 1, boiling at 155°—160°.
No. 2, " " 171°—172°.
No. 3, " " 185 —190.

The base boiling at 171°—172° was the most considerable in quantity and is the only one whose study has been completed. Its formula derived from analysis and estimation of vapor density is $C_7H_{10}N_2$ having the theoretical composition—

C, 68.85 per cent.
H, 8.20 per cent.
N, 22.95 per cent.

This base is very soluble in water, ether and alcohol. When pure it is a liquid, very mobile, colorless, with high refractive power, with a characteristic nauseous odor.

It is almost neutral to litmus. Its density at 12° is .9826.

With $PtCl_4$ it gives a well crystallized chloro-platinate, soluble in water and alcohol. The best reagents for detecting this base are phosphotungstic and phosphomolybdic acids. The former reagent gives an immediate white precipitate even in $\frac{1}{10000}$ solutions, the latter a yellow precipitate in the same conditions. H. W. W.

Toxic Properties of the Organic Bases in Alcohols.—Robert Wurtz (Comptes rendus, Vol. 106, pp. 363-4) has made some physiological tests with the base above described ($C_7H_{10}N_2$) on frogs, guinea pigs and rabbits.

The dose required to kill a guinea pig varies from $\frac{1}{800}$ to $\frac{1}{1200}$ of the weight of the animal.

Soon after the injection of the dose the animal becomes stupefied. At the end of 15 min. there is partial posterior paralysis. Sensibility becomes diminished, the pupil is dilated and insensible to light, the heart's action is diminished and the temperature falls to 35°. Death follows coma more or less prolonged. H. W. W.

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Choline in Germinating Seeds.—By Brieger's method, choline has been obtained from germinating pumpkin sprouts. Only three grams of the aurochloride was obtained from a kilogram of the dried sprouts. Schulze in Zeitschr. f. physiolog. Chemie, B 11, S. 365.

Action of Gaseous Poisons.—By examining the ear of the rabbit with the spectroscope, the changes produced in the spectrum of the blood by gaseous poisons may be observed. In poisoning by carbon monoxide the compound of that substance with haemoglobin may be plainly recognized. But the hydrocyanic acid compound studied by Beyer could not be detected. Nitrous oxide seemed to have no action on the blood, while nitric oxide caused rapid reduction of the oxyhæmoglobin, but gave no evidence of the formation of a compound, such as is observed by treating the blood outside of the body with the gas. Ammonia, even when sufficiently dilute to be easily respirable, rapidly reduces the oxyhæmoglobin. The same is true of hydrogen sulphide. Belky in Chem. Centr. 1886, 887.

Detection of Arsenic.—Bring the liquid to be tested in contact with brass, when a gray deposit will be formed, if arsenic be present. Heavy metals, even iron, must be absent. Pure hydrochloric acid must be added to the liquid until it amounts to from 5 to 15 per cent. If much arsenic be present, it is sufficient to place a drop of the liquid on a brass plate and warm gently, and after a minute or two, the plate may be rinsed with water and examined. For minute traces the rinsing of the plate should be omitted. One part of arsenic in 80,000 will give a gray film in half an hour; one in 250,000 in an hour. If 1¼ hours elapse without any deposit, arsenic may be regarded as absent. If antimony be suspected it is better to immerse a strip of brass in the liquid and either warm or set aside at the ordinary temperature for some hours. Arsenic gives a steel-gray to black film which volatilizes on being heated in a spirit lamp. After turning steel-blue, antimony gives a light-grey deposit, which remains unchanged on being heated. Hager in Chem. Centr. 1886, 680.

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The Dearsenification of Hydrochloric Acid and Reinsch's Test.—Copper foil used for the dearsenification of hydrochloric acid must have a clean, bright surface. That which has already been used for this purpose may be scoured with sand and used again. Copper containing traces of arsenic may be used, as the arsenic in the copper exists in the form of an alloy which is not attacked by acid.

Before using copper in Reinsch's test the following procedure should be carried out: Immerse a piece of perfectly bright foil in perfectly pure hydrochloric acid of from 10 to 12.5 per cent., and allow to remain for two hours; if at the end of that time it is still bright and free from deposit it may be used. The foil may contain traces of arsenic and still give no coloration with arsenic.

For the detection of arsenic in copper Odling's method is recommended. This consists in distilling the copper with iron oxide or chloride; volatile arsenic chloride passes over and may be found in the distillate.

Or, a rapid and reliable test for arsenic in copper is to place a drop of ammonium hydrate on the bright metal, allow to remain 30 minutes, wash off with water and dry with a cloth; then place a few drops of dilute acetic acid on the spot, allow to remain ten minutes, wash with water and dry with a cloth. If the copper contains traces of arsenic, a gray coloration is seen on the spot treated. This is a very sure test. Hager in Chem. Centr. 1886, 772.

Haemidin Crystals.—The crystals obtained by the method of Danneberg in testing blood stains deposited on iron are now shown to consist of sulphur and the test is thereby shown to be worthless. Amthor in Chem. Zeit. B. 10, S. 1479.

Color Reactions of Arsenic.*—Arsenic anhydride mixed with catechol gives a gray-green color, which changes to amethyst. In this way it is distinguished from phosphoric anhydride, which gives no coloration. With arsenic anhydride resorcinol and quinol give respectively a sepia and a yellowish

*This Journal, 1, 201.

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coloration, and this reaction may be used to distinguish between these three phenols. With catechol, arsenites give a flesh tint, which distinguishes them from the arsenates. Levy in Compt. Rend. 7, 103, p. 1195.

Composition of Strychnine.—In order to obtain evidence in regard to the view of Hanssen that strychnine contains a phenylpyridine group as well as a quinoline group, strychnine was distilled with alkalis and not only a hydride of pyridine but γ-picoline was obtained. Endeavors to obtain methyl chloride by the decomposition of strychnine were unsuccessful. Stoehr in Berichte, B. 20, S. 810.

PHYSIOLOGICAL CHEMISTRY.

Examination of Urine for Lead in Cases of Suspected Chronic Lead Poisoning.—E. S. Wood, Therapeutic Gazette, 12, 138, "The urine is strongly acidulated with nitric acid, and evaporated to dryness upon a water or steam bath. If a sufficient amount of nitric acid has been added the residue left will be of a light yellow color; if it is not more nitric acid must be added to the residue and the evaporation continued. When the residue is dry, or nearly so, it may be transferred to a crucible and ignited by gentle heat, or the evaporating dish containing the residue may be transferred to a sand bath and heated, when ignition takes place very quickly, with more or less deflagration. If proper care be taken in managing the heat there will be no loss of material on account of the deflagration, and a perfectly white residue will be left. After cooling, this residue is extracted with hot, dilute HCl, filtered while hot and the filtrate precipitated with ammonium hydroxide and ammonium sulphide; this precipitate is washed by decantation three or four times with boiling water, then acidulated with HCl, to dissolve the phosphates and sulphide of iron, and allowed to stand until the next day to settle. The precipitate, which will contain sulphide of lead, if any lead was present in the urine, is collected upon a small swe-

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dish filter paper (or other filter free from any trace of iron), washed thoroughly with boiling distilled water, and treated while on the filter with hot *dilute* pure nitric acid, which liquid is collected in a watch glass, and evaporated to dryness on a water bath. This residue, which contains any lead present in the form of a basic nitrate, is treated with a drop of water and a crystal of potassium iodide as a *preliminary* test for lead ; if lead is present, there will be a yellow streak of iodide of lead. A colored streak may also be produced if the residue contains compounds of other metals, especially copper, bismuth, or iron (compounds of the last metal sometimes becoming introduced in traces in the form of dust, or as a contamination in the filter). If a colored streak has been produced, the residue containing it is moistened with a drop of acetic acid, and washed with boiling distilled water into a small filter, the filtrate being collected in a test-tube (perfectly clean) ; a few drops of dilute sulphuric acid are then added, the test-tube stoppered, and placed aside until thoroughly settled. If any lead be present, it will be converted into the form of sulphate of lead, which will form a sediment at the bottom of the test-tube, often in so slight an amount that it cannot be seen until the test-tube is gently moved, so as to cause the fluid within to rotate, when the sulphate of lead precipitate will be drawn up in the center of the fluid in the form of a cone, when it can be easily seen even when present in very minute amount.

Every precaution so far as apparatus and chemicals are concerned, is taken. The crucibles used are Berlin crucibles, and both evaporating dishes and crucibles have been found, by repeated analyses, not to yield any lead. The final test being the formation of sulphate of lead, avoids any possibility of error due to the presence of traces of copper or bismuth, which would certainly exist if reliance were placed upon the color reaction with potassium iodide. * * * In well-marked cases of chronic lead poisoning, even while the patient is being treated with potassium iodide, the amount of lead eliminated with the urine is very small, never exceeding a very few milligrams in 24 hours, and in the majority of ca-

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ses being only a small fraction of a milligram. The successful detection of lead in one or two liters of urine in such cases requires, therefore, that the process used should be a very delicate one, and also that it should be conducted with the greatest care." E. H.

NOTES.

Tin Containing Mercury. Dr. R. Kayser reports a case of mercurial poisoning from mercury volatilized in the melting room from molten tin. A sample of the metal contained as much as 1.3 per cent. mercury. The tin seems to have been obtained from the residue of a mirror manufactory. *See Chem. Zeit.* **12**, 151.

—E. Bauer finds that traces of eugenol and vanillin occur in commercial alcohol, especially in the variety made by the fermentation of molasses. Ibid.

—Prof. J. B. Mackintosh of Lehigh University has accepted a position with the Consolidated Gas Co., New York City.

—Mr. H. H. Harrington has been appointed Acting Professor of Chemistry and Physics at the Agricultural and Mechanical College, College Station, Texas.

NECROLOGY.—On Nov. 21, 1887, August Stromeyer, a German chemist, known chiefly by his contributions to analytical chemistry.

—On Nov. 6, 1887, in Berlin, A. Geyger committed suicide by taking strychnine.

—On Oct. 17, 1887, in Berlin, G. R. Kirchhoff. Kirchhoff's name will always be associated by chemists with that of Bunsen in their work upon Spectrum Analysis. Most of his investigations belonged to Physics, in which he was an indefatigable worker and greatly honored.

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—On Nov. 12, 1887, Paul Casamajor, chemist of Havemeyer and Elder and sometime corresponding secretary of the American Chemical Society. Mr. Casamajor was born at Santiago, de Cuba in 1831, and studied chemistry at Harvard and in Paris. He first settled in New York, then removed to the oil regions of western Pennsylvania, returning to New York in 1866. He then entered the employ of Havemeyer and Elder, sugar refiners, and was still in their employ at the time of his death. Mr. Casamajor was occupied during the latter part of his life upon the filtration of sugar liquors and greatly improved this part of the process. The above facts are taken from a notice by Dr. Endemann, printed in the Journal of the American Chemical Society. E. H.

—James Reynolds Duggan, Prof. of Chemistry, in Wake Forest College, N. C., died on Jan. 8th, 1888. Dr. Duggan was born Nov. 14, 1859, in Washington county, Ga., educated at Mercer University in the same state, and afterwards studied at the Jefferson Medical College, where he graduated in 1879, and at Johns Hopkins University, where he was appointed Fellow in Chemistry and received the degree of Ph. D. in 1884. In 1886 he was called to Wake Forest College and superintended the building of a new laboratory there. Dr. Duggan was a man of great promise and his untimely death causes deep regret. He investigated the influence of alcohols upon the conversion of starch by diastase, the determination of absolute neutrality, and did considerable work in fementation and bacteriology. He was employed by the commission appointed by the government to investigate the manufacture of glucose and by the American Public Health Association in an examination of the value of disinfectants. E. H.

—Professor Byron W. Cheever, metallurgist at the University of Michigan, died in Ann Arbor on Mar. 6, 1888, after an illness of only a few days. On Feb. 27 he returned from a rapid professional visit to Arizona, in the examination of mining lands, and shortly after his arrival was attacked with

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a typho-malarial fever, the violence of which his bodily powers were unable to resist.

Professor Cheever was born in Ellisburg, Jefferson county, N. Y., Sept. 17, 1841. He entered the University of Michigan in 1859, graduating in Arts in 1863, afterward taking continued studies in chemistry at the same institution, where also he obtained a degree in medicine in 1867. He then engaged, successively, as an analytical and metallurgical chemist in Philadelphia, an analyst of fertilizers in the West Indies, and then for a longer period as a practical miner and metallurgist in the Rocky Mountains, where he gained great practical acquaintance with workable mineral deposits. Suffering in health from the injurious vapors of retorting works, he returned to Ann Arbor in 1874, and, a few years afterward, he accepted a position in the corps of teachers of the chemical laboratory, being appointed to the chair of metallurgy in 1881.

In experimental investigation he was careful of all conditions, rigid in his directions, and conservative in the adoption of conclusions. As a teacher he held his students to exactness in results, and to a clear understanding of principles. His contributions have a permanent place in chemical literature, as evidenced on the pages of this and other periodicals.

A. B. P.

—Elwood Alexander Schultz, Tutor in Chemistry, Lafayette College. Born Oct. 14, 1864, died March 23, 1888. Mr. Schultz worked on the nitro products obtained from bituminous coal and obtained interesting results, which were, however, not ready for publication at the time of his death. He was a young man of most engaging social qualities and his early death is much regretted by his associates. E. H.

—On April 8, 1888, Prof. A. W. Hofmann. No sufficient account of Hofmann's work can be given here from lack of space; a brief sketch will be found in the Chemiker Zeitung **12**, 471. Few men have made so great an impress upon chemical science as Hofmann. He was an indefatigable worker and needs no monument other than his works.

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NEW BOOKS.

SKELETON NOTES UPON INORGANIC CHEMISTRY.—Part I, Non-Metallic Elements, by P. de P. Ricketts, Ph. D. and S. H. Russell, E. M., $1.50; John Wiley & Sons. The elements are given alphabetically. Under each the history, occurrence, preparation, properties, detection, applications, and principal compounds. Sufficient space is left for additional notes. The paper, printing and binding are good.

SIXTH ANNUAL REPORT OF THE N. Y. AGRICULTURAL EXPERIMENT STATION, for the year 1887. Dr. Babcock reports upon the Butters for the New York dairy show. He finds while these butters differ widely in the amount of volatile acids, there seem to be no differences which can be attributed to breed. * * The extreme variation is from 11.5 c. c. to 16.1 c. c. The average for all determinations being 13.95 c. c. The amount of olein as determined by the iodine absorption varies from 27.7 to 52.1. The Holstein butter contains a large proportion of olein, the average being 46.19, that for the other cows tested being 35.4. The extremes in melting point determined by Wliey's method * are from 30.5 to 36.9° C.; these extremes are so wide as to render the test of no value in detecting adulteration; the best test for this purpose he finds to be the determination of the viscosity of a solution of the potassium soap. The amount of sterine in butter has been much over-estimated; it is probably less than tree pehr cent. in most butters. Dr. Ladd gives methods for the estimation of sugar, starch and ash constituents in fodder which is reprinted in this number, (p. 145).

PAMPHLETS RECEIVED.—Proceedings of the Michigan State Phamaceutical Association for 1887, (from Prof. Prescott).

—Report of the Penna. State College: Agricultural Chemistry and Agricultural Experiment Work for the year 1886.

—Annual Report of the Connecticut Agricultural Experiment Station for 1887.

* This Journal 1, 39.

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—California State Mining Bureau. Wm. Irelan, Jr., State Mineralogist. Seventh Annual Report of the State Mineralogist for the year ending, October 1, 1887.

—Fifth Annual Report of the State Agricultural Experiment Station at Amherst, Mass., 1887.

—The First Quarterly Report of the Michigan State Laboratory of Hygiene. By Prof. V. C. Vaughan, M. D., Ph. D.

—Twenty-ninth Annual Report of the Inspector of Milk and Vinegar for 1887, Boston. Rockwell & Churchill.

—Mass. Agrl. Exp. Station Bulletin, No. 28, March, 1888.

—Methods of Sanitary Water Analysis, with an Examination of the Water Supply of Cleveland. By Albert W. Smith.

—The Loco Weed. By E. L. Sayre, Ph. G. Reprinted from Trans. Kansas Acad. of Sci.

—Notes of Work of Students of Practical Chemistry in the Laboratory of the Univ. of Va. By F. P. Dunnington. Reprinted from Amer. Chem. J., Vol. X, No. 1.

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VOL. II. [JULY, 1888.] PART 3.

THE

Journal of Analytical Chemistry.

FILTRATION WITH FILTERS OF METALLIC FELT.

BY CHARLES E. MUNROE.

GOOCH'S admirable filter of asbestos felt* is too widely known and extensively used to require description, and his ingenious modification of it in which volatile felts† are employed is recognized as forming a useful extension of the method for certain applications. Some time since it occurred to me that another modification might be wrought if we were to use, for the manufacture of the felts, metallic salts which were easily decomposed on ignition and which, when decomposed, left the metal as a spongy coherent residue. Such a salt is found in the ammonium platinic chloride and by its use I have obtained a metallic felt which served very nicely for this purpose.

To produce this filter I precip.tated platinum chloride with ammonium chloride, using a slight excess of the reagent, and washed the salt thoroughly, first with water and then with alcohol. Then taking a Gooch filtering crucible of platinum I placed it on a thick piece of bibulous paper and poured in the moist salt. The alcohol ran through the perforations in the crucible and was absorbed by the bibulous paper while the salt remained behind, the filtering crucible being filled in this way to a height of about 5 mm. The crucible was then carefully cleaned and dried, the cap and cover put on, and the whole ignited, thus driving off the volatile constituents and leaving a spongy coherent residue of metallic platinum well distributed over the perforated bottom of the crucible. In order to prevent the sponge from cracking and curling it was

*Proc. Am. Acad., 1878, p. 342.
†Proc. Am. Acad., 1885, p. 390.

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found essential to dry and ignite the salt quite cautiously but in some instances where cracks did appear they were easily and effectually closed by gently rubbing with a glass rod, while in other cases the crevices were filled with a fresh portion of the ammonium platinic chloride and the drying and igniting repeated. The latter method was also employed when it was thought desirable to increase the thickness of the felt. After a short trial the preparation of the felt becomes quite easily and readily accomplished. The prepared filters are used in the same way as Gooch's asbestos filters are, the caoutchouc gasket described in my paper on the "Use of Porous Cones in Filtration,"* being employed to secure an air-tight joint. The platinum felt may be easily removed, when desired, by means of a spatula, the small portions remaining in the perforations being pushed out with the point of a needle.

I have repeatedly prepared these filters in the manner above described and have filtered with them such preparations as freshly precipitated barium sulphate to my entire satisfaction. Not only that but by treating the precipitates with their proper solvents I have been able to clean the felt so that the same filter could be used repeatedly. The following data illustrates such use of this filter :

Weight of crucible and felt after first ignition	31.0612	grms.
" " " second "	31.0607	"
" " " rubbing with glass rod to remove thin spots	31.0607	"
Weight of crucible and felt after third ignition	31.0607	"
Weight of ditto after 250 cm. of water have been passed through ten times	31.0607	"
Weight of ditto after freshly precipitated CaC_2O_4 has been filtered upon it and ignited	31.5385	"
Weight of ditto after treatment with HCl washing and igniting	31.0634	"
Weight of ditto after same operation repeated	31.0609	"
" " " " "	31.0608	"
Weight of ditto after $BaSO_4$ has been filtered upon it and ignited	31.4403	"

*A. J. Sci. 1, [3] May 1871.

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Weight of ditto after dissolving the $BaSO_4$ in hot, concentrated H_2SO_4 . . . . . 31.0640 grms.
Weight of ditto after second treatment with H_2SO_4 . . . . . 31.0609 "
Weight of crucible complete . . . . . 30.6744 "
Weight of felt . . . . . .3863 "

Felts of this character may of course be obtained by similar means from easily decomposable salts of other metals than platinum and such felts may be found to have useful applications.

It is probable that this method of producing a platinum sponge within a platinum tube may find useful applications in organic chemistry in addition to its use as a filter.

TORPEDO STATION, NEWPORT, R. I.

ON THE SOLUBILITY OF THALLOUS IODIDE, AND THE DETERMINATION OF THALLIUM.

BY J. H. LONG.

Among the several methods proposed for the determination of thallium that by precipitation as thallous iodide is the most convenient and in most cases probably the most accurate. This statement presupposes that the solubility of the iodide in several menstrua is well known and properly allowed for. This, however, is not quite the case, and in view of the fact that different solubilities have been assigned to the iodide by different authorities, I have thought it worth while to carry out a new set of experiments on the subject. An investigation of this nature suggested itself to me in the course of some work with dilute solutions of thallous salts where a knowledge of the exact percentage strength was important.

Crookes gave the solubility as 1 in 4453 parts of water, at 17.2° C., and stated that in solution of potassium iodide it is even more soluble. Hebberling gives the solubility as 1 in 11676 parts of water at 16°C., while Lamy and Descloizeaux

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place it at 1 in 16000 parts at the same temperature. According to Hebberling the solubility in 98 per cent. alcohol is 1 in 18934 parts at 19°C.

Some of the text books state that the solubility in dilute ammonia water is less than in pure water. I have carried out experiments with a view of throwing light on these several points.

For my tests I employed pure thallium sulphate prepared by solution of the pure metal in dilute sulphuric acid, and evaporation. The crystals obtained were further purified by two crystallizations from water and finally dried over strong sulphuric acid. An amount of this sufficient for all experiments was precipitated by a slight excess of potassium iodide, free from traces of chlorides and bromides, washed thoroughly with water and dried gradually at first, and finally at a temperature of 120°C. It was then transferred to a stoppered bottle for use.

The tests were in most cases carried out by digesting a gram of this with water for the required time at a temperature of 20°C. The undissolved portion was transferred to a Gooch filter, dried thoroughly and weighed. The asbestos employed in the filter was an excellent sample, being quite insoluble in the liquids passed through it and showing no change whatever in weight after being heated to different temperatures.

It seems to me that the loss in weight of the thallous iodide, found in this way must be a practically useful measure of its solubility.

A. SOLUBILITY IN WATER.

1. Digested 1 gm. one hour in 400 c. c. and transferred to filter, using 100 c. c. more. The loss found after drying was .0279, from which solubility = 1 in 17921.

Washed the residue on the filter and found a loss of .0195, from which solubility = 1 in 25641.

2. Digested 1 gm. one hour and washed on filter, using in all 510 c. c. Found a loss of .0360, from which solubility = 1 in 14166.

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The filter-pump was then operated very slowly and three portions of water of 500 c. c. each were passed through, the loss being determined each time.

The first 500 c. c. passed in two hours. Loss .0220. Solubility = 1 in 22727.

The second 500 c. c. passed in two hours. Loss .0239. Solubility = 1 in 20920.

The third 500 c. c. passed in one and one-half hours. Loss .0180. Solubility = 1 in 27777.

3. Digested 1 gm. seventy-two hours in 500 c. c. of water, transferred to filter by means of 20 c. c. of water The loss was .0310. Solubility = 1 in 16774.

Washed on the filter as above. The first 500 c. c. passed in two and one-half hours. Loss .0260. Solubility = 1 in 19321.

The second 500 c. c. passed in two hours. Loss .0190. Solubility = 1 in 26316.

4. Digested 1 gm. twenty-four hours in 500 c. c. of water; transferred to filter with 40 c. c. of water. The loss was .0300. Solubility = 1 in 18000.

Washed on the filter with 500 c. c. of water, in two hours, this residue lost .0225. Solubility = 1 in 22222.

5. Digested 1 gm. nine days in 500 c. c. of water. Transferred with 30 c. c. The loss amounted to .0280. Solubility = 1 in 17857.

The solubility during digestion with water appears, therefore, to be about 1 in 17000, while that in washing is somewhat less.

B. SOLUBILITY IN 90 PER CENT. ALCOHOL.

1. Digested 1 gm. one hour in 500 c. c. of alcohol having a strength of 90 per cent. by weight. Transferred to the filter with 50 c. c. Loss .0020. Solubility 1 in 275000.

Washed this residue three times with strong alcohol, using 500 c. c. each time. The loss in each case was .0010, from which solubility = 1 in 500000.

2. Digested 1 gm. one hour in 500 c. c. of alcohol and

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transferred with 30 c. c. The loss was .0020, from which solubility = 1 in 265000.

3. Digested 1 gm. one hour in 1000 c. c. of alcohol and transferred with 90 c. c. The loss was .0042. Solubility = 1 in 238095.

Washed the residue during two hours with 500 c. c. of alcohol, causing a loss of .0010. Solubility = 1 in 500000.

C. SOLUBILITY IN 50 PER CENT. ALCOHOL.

Digested three portions of 1 gm. each with 500 c. c. of alcohol, stirring thoroughly, and transferred to filter with 50 c. c. of alcohol. The losses were—

.0132	solubility=1 in 41666
.0172	" =1 in 34884
.0155	" =1 in 35484

The last residue washed on the filter during two and one half hours with 500 c. c. of 50 per cent. alcohol lost .0097. From which solubility=1 in 51546.

A further washing with 250 c. c. during three hours gave a loss of .0049. Solubility=1 in 51020.

D. SOLUBILITY IN AMMONIA WATER.

1. Digested 1 gm. one hour in 500 c. c. of ammonia solution of 6.5 per cent. strength, using 40 c. c. in transferring to filter. The loss was .0410. Solubility=1 in 13120.

2. Digested 1 gm. one hour in 500 c. c. of same. using 50 c. c. in transferring. The loss was .0415. Solubility=1 in 13253.

When the residue was washed on the filter with 500 c. c. during two hours the loss was .0395. Solubility=1 in 12658.

3. Digested 1 gm. one hour in 500 c. c. of ammonia water of 2½ per cent. strength. The loss was .0415. Solubility= 1 in 13132.

4. Digested 1 gm. one hour in 500 c. c. of solution of 1¼ per cent. strength, using 35 c. c. in transferring. Loss. 0315. Solubility=1 in 16984.

E. SOLUBILITY IN A 10 PER CENT. KI SOLUTION.

1. Digested 1 gm. one hour in 250 c. c. of solution and

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washed thoroughly on filter with 125 c. c. of 50 per cent. alcohol until free from KI. The loss was .0020.

2. Digested 1 gm. twenty-four hours in 100 c. c. of solution and washed the residue with 100 c. c. of 50 per cent. alcohol. The loss was .0015.

After deducting the amount dissolved by the alcohol used in washing, the solubility in the iodide solution seems to be practically zero.

According to the above experiments the solubility is somewhat less than usually given. As one would naturally expect less is dissolved during washing on the filter than during digestion in a beaker.

Without doubt, slightly greater quantities could have been dissolved by prolonged digestion at a higher temperature, but here I am chiefly interested in determining how much is soluble under the conditions which would obtain in the practical analysis of a thallous salt. It will be noticed that during slow washing with strong alcohol the solubility reaches the small fraction of one part in 500000.

Of course it would be seldom possible to precipitate from an alcoholic solution of this strength, and perhaps not often practicable to wash with such alcohol, because of the slight solubility of salts to be removed. But precipitation from alcohol of 50 per cent. strength is generally possible when desirable, and the solubility of the iodide here is so slight that for most purposes it can be neglected. In washing with alcohol of this strength the solubility can safely be taken as 1 in 50000.

Thallous iodide seems to be quite insoluble in a 10 per cent. solution of potassium iodide, and is only very slightly soluble in a solution much weaker than this, as I found in previous experiments not given here.

I give here a few illustrations of precipitations by means of potassium iodide.

A. Dissolved 1 gm. of pure Tl_2SO_4 in 50 c. c. of water and added 10 gm. of KI in 50 c. c. of water. The mixture was

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heated to boiling and allowed to cool before being filtered. The precipitate was finally washed with 175 c. c. of 50 per cent. alcohol.

	Found. Tl I.	*Theory.*
1st.	1.3120	1.3124
2d.	1.3110	

In this case it will be observed that the great excess of KI seems to prevent much solution of the precipitate, even during washing. The washing was continued only long enough to remove the last traces of KI.

B. Dissolved 1 gm. of pure dry $HTlC_4H_4O_6$, in fine crystals, in 250 c. c. of water. Precipitated with a slight excess of KI and allowed to stand an hour. Filtered and washed the precipitate with 100 c. c. of 50 per cent. alcohol, dried and weighed.

	Found. Tl I.	*Theory.*
1st.	.9338	.9364
2d.	.9332	

In this case the excess of precipitant was only slight and allowance must be made for the solubility in the weak alcohol. Adding 1 part for 50000 as suggested above, or .002, we obtain very nearly the theoretical yield.

In presence of an excess of another tartrate the solubility of the Tl I seems to be slightly increased.

The experiments detailed above show that there is no advantage in precipitating in presence of free ammonia; in fact this seems to increase rather than diminish the solubility of the thallous iodide. For practical purposes it is sufficient to precipitate the warm concentrated solution of the thallous salt with a slight excess of KI, allow to cool thoroughly, filter and then wash with alcohol of 50 per cent. strength. The use of the Gooch filter is to be highly recommended here.

Most of the above tests were carried out by my assistant, Mr. Mark Powers, to whom my thanks are due.

CHICAGO, MARCH 30, 1888.

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A METHOD FOR THE DETERMINATION OF MANGANESE IN STEEL.

By Frank Julian.

In the following modification of a well-known method for the rapid estimation of manganese in steel, the filtration of the precipitated binoxide, which is very apt to be tedious and unpleasant, is avoided by titration in the solution itself. Either oxalic acid or ferrous sulphate may be employed for solution of the MnO_2, with equally good results; but the use of the latter, as here described in detail, seems preferable for several reasons.

The solution of the steel is prepared by dissolving one gramme in a 10-oz. casserole with 20 c. c. of nitric acid of sp. gr. 1.2; concentrating to a small volume, and adding about 30 c. c. of colorless concentrated nitric acid.

In precipitating the manganese from the boiling solution, care must be taken to add no more potassium chlorate than will just cause the yellow fumes to disappear, showing that the precipitation is complete. The solution is then boiled gently, keeping the casserole well covered to prevent too much evaporation, for five minutes or more, until all chlorine is expelled; then cooled and the liquid with the precipitate poured into 400 c. c. of cold distilled water contained in a 24-oz. beaker, and twenty-five c. c. of ferrous sulphate solution (4 grammes Fe or 28 grammes $Fe(NH_4)_2\ 2SO_4$ cryst. per liter) added. After removing the small amount of MnO_2 adhering to the casserole by rinsing with a portion of the liquid, the solution is ready for titration with permanganate of potassium (1.5 grams per liter).

In standardizing the permanganate, it is necessary that about the same amount of water, nitric acid and ferric nitrate be present as in the actual analysis; as these slightly increase the quantity of permanganate required for ferrous sulphate alone.

The results obtained seldom differ by more than three or four hundreths of one per cent., and agree well with gravimetric work. For low-manganese steel it is well to take two grammes or more for analysis.

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MANUFACTURE OF CUPELS.

By Francis C. Blake.

The apparatus described below is now in use for the making of all sizes of boneash cupels used in assaying at the works of the Pennsylvania Lead Company.

It works rapidly and easily and turns out cupels that are very uniformly compressed and that give under similar conditions exceedingly regular silver absorptions which are as low as those of the best hand-made cupels, or of cupels that we have tested, made by other machines.

The cupel pressing machine is a No. 7 upright lever press of the regular style, made by the E. W. Bliss Co. of Brooklyn, N. Y. Lever presses that could be easily adapted to the work are made by several other manufacturers. The press is shown

Fig. 1.

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by Fig. 1. The opening at the center of the bed-plate is filled by a removeable plug made flush with the plate. Planks are fitted around the bed-plate and the back part of the press forming a table, 38 x 48 inches, with the press in the center. This arrangement is shown by Fig. 2, which is taken from a photograph.

On each side in front are boxes for holding boneash and the tools not in use. A guard extends around the table, except over the boxes, to prevent the wasting of boneash.

The male dies, one for each size of cupels made, are of hard brass turned to shape and polished. The style known as the western pattern being used. They are easily secured in the press slide. The molds in which the cupels are formed are

Fig. 2.

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shown on the press table in Fig. 2. They are made of hard brass and open like scissors. The boneash was found to adhere somewhat to iron which was at first tried for both dies and molds. The pressed cupel drops out at once upon opening the molds. Three stops, having adjustment screws in each, are screwed into the bed-plate of the press—one at each side of the center and one at the back—so that the scissors mold is held shut by the side stops and comes into place directly under the die when the end of the mold touches the back stop.

The operation of making the cupels is as follows: The mold is held shut in one hand, filled with boneash by the other hand of the operator and then shoved into place under the press slide and by a single movement of the foot lever the cupel is pressed. The mold is then withdrawn, opened and the cupel is placed on the drying tray.

The machine has not been tested for speed, but from three to four hundred cupels per hour can easily be made with it.

The use of a foot lever press and opening molds are decided improvements upon hand screw presses and solid molds.

The power or leverage of the press can be changed in several ways, as is shown in Fig. 1, but ordinarily we use the press with the lever pin as shown in Fig. 2. If very large cupels are to be made the pin is moved to one of the front holes.

We find that it is desirable to purchase boneash in large lots and to thoroughly mix the whole lot before using in order that the working of the cupels shall be as uniform as possible. We often can obtain better cupels by mixing together different lots of boneash. For example we are now using with the best results a mixture of boneash part of which was purchased in Denver and a part of it in New York. The results are better with the mixture than with either brand alone, though both are stipulated to be the best obtainable by the dealers in assay materials.

Of the two, the Denver boneash is the cheaper and a trifle

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the better. From a sample of the Denver boneash 5 per cent. would not pass through a No. 80 sieve and 12 per cent. remained on a No. 100 sieve; of the boneash from New York all but 0.75 per cent. passed through the No. 80 and only 7.5 per cent. remained on the No. 100 sieve. In respect to uniform grinding the latter boneash is the better, but it is on the whole a little too fine.

The best boneash should, I think, all pass through a No. 80 sieve, but there should be a considerable proportion of it that will not pass through a No. 100, perhaps one-fourth or one-fifth.

The Denver boneash contained less of the carbonate or oxide of calcium, which have a tendency to increase the silver absorption of the cupel and also render it more liable to crack at the center and at the edges, especially when hard lead bullion is being cupelled.

Some cupels made of ground apatite gave especially good results in cupelling lead containing considerable copper and antimony. The first antimonial litharge being much better absorbed than by the boneash cupels and the edges of the cupels were not cracked in the least. The silver absorption was about the same as with the boneash.

Magnesia added to the boneash has a less injurious effect than lime. We shall make some further tests with apatite cupels to see if mineral less pure than the small sample we had for trial will give good results. If such is the case it will make a useful material for cupels used for assaying very impure lead bullion. The boneash, free from absorbed litharge, recovered from cupels that have been used, we find by careful tests to be as good as the fresh material if it is properly sifted.

We find, as is generally known, that cupels improve by being made some time before they are used and we carry 7000 to 8000 in stock, sufficient for over two months work.

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THE METHODS OF MECHANICAL SOIL-ANALYSIS.*

PART II.

By Thomas B. Osborne, Ph. D.

In the report for 1886 were given the first results of an investigation of the methods of mechanical soil-analysis. The method of Knop as modified by Moore and that of Hilgard, as well as one developed in the Station laboratory were there discussed and compared. Since then the investigation has been extended to Schöne's method, and to the process of Schlösing, which combines chemical and mechanical treatment.

These methods comprise all hitherto proposed that now appear to be worthy of investigation; the others, such as Schulze's, Nöbel's, Müller's, Kühn's, Masure's and others, either employ conical elutriating vessels, which as Hilgard has pointed out and this investigation fully confirms, give wholly incorrect results, or they are methods depending on subsidence through a given height of water for a definite length of time, a principle which experience has shown is not adapted to yield results of value with any certainty whatever.

SCHÖNE'S METHOD.

The apparatus used, obtained from Müncke, of Berlin, was similar to that described and figured by Schöne (Zeitschrift f. analytische Chemie, **7**, 1868, p. 29), with the addition, suggested by Orth, of a second elutriating tube having a di meter one-half that of the Schöne tube.† Water was supplied to the apparatus under a constant pressure by means of a Mariotte's bottle.

Schöne's elutriator has been so frequently described that any further reference to its construction is unnecessary. The hydraulic values of the different currents used were not directly determined but the flow of water was so regulated as

* From Report Conn. Agrl. Exp. Station for 1887. See this Journal **1**, 252.

† Die Agronomische Bodenuntersuchungen und Kartirung, von Dr. Max Fesca, Berlin, 1879, pp. 19 and 143, also Albert Orth, Ueber mechanische und chemische Bodenanalyse. Ber. xv, p. 3026.

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to carry off only such particles as had diameters equal to or less than the upper limit of the grade to be separated. It was thus easy to obtain results strictly comparable with those given by the other methods used.

In the first trial made, the soils were subjected to no preparatory treatment beyond simple sifting. The samples were neither boiled with water nor acted on by hydrochloric acid nor by alkali-solutions.

Schöne, in his original paper, following Schübler and Schulze, prescribes boiling as a needful preliminary in all cases. Clayey soils containing much humus he says should be boiled an hour with water containing in solution 1-2 per cent. of alkali hydroxide. Sandy soils he directs to free from organic matters by ignition, and calcareous earth he recommends to treat with cold dilute hydrochloric acid to remove carbonate of lime.

As serious objections may be urged against all these last mentioned modes of preparation, it was determined to make some trials on the simply sifted earth, in order to gain an idea of the extent to which the soil could be differentiated without their aid, the results of applying the method of Beaker elutriation being employed as standards of comparison.

Twenty grams of the air-dry soil were sifted under water through a quarter-millimeter sieve. The fine material which after passing the sieve remained suspended in the water was poured into the Schöne tube, the coarser portion being rinsed into the Orth tube. The water current was then regulated so that the largest particles of quartz carried off had an average diameter of $.01^{mm}$.

When the current ceased to remove any appreciable quantity of the soil its velocity was increased so that the largest quartz grains passing over had a diameter of $.05^{mm}$. These portions were collected in separate vessels.

As Hilgard noticed in the case of Schulze's elutriator, secondary currents formed during the process of elutriation which descended along the walls of the conical part of the

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Schöne tube and for some distance along the sides of its cylindrical portion. The result of these currents was to produce globular aggregates of small particles which fell to the bottom of the tube. These flocculæ could be to some extent broken up by turning on from time to time for a few seconds a rapid current of water, but a very considerable proportion of them remained unbroken to the end of the elutriation and were only moved forward when the current was increased so as to carry off the coarsest grade.

SOIL FROM GARDEN OF THE EXPERIMENT STATION.—NOT BOILED.

ANALYSES WITH THE SCHÖNE–ORTH ELUTRIATOR.

	A.	B.
Above .25^{mm}	48.82	48.82
.25—.05^{mm}	27.36	29.94
.05—.01^{mm}	8.63	6.07
.01— 0^{mm}	7.36	7 31
Clay (by difference)*	1.00	1.03
Loss on ignition	6.83	6.83
	100.00	100.00

The coarser products obtained in these analyses, under the microscope were seen to contain material finer than properly belonged to them. The various sediments of A were therefore subjected to systematic beaker elutriation and the finer material thus readily separated was in each case weighed and its quantity added or subtracted as required to make the obvious corrections. The following figures show the outcome of this correction compared with the original analysis and with the results of direct beaker elutriations.

* "Clay," as given in this and in the other analyses by the Schöne and Beaker methods instanced in this paper, is, in accordance with Hilgard's conventional method, that part of the grade having diameters of from .01–0^{mm} which remains suspended after 24 hours' sedimentation from water having a depth of 200^{mm}.

Neither Schöne nor the various experimenters who have employed his method in analysis of soils appear to have undertaken to subdivide the grade .01–0^{mm}.

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SOIL FROM GARDEN OF THE EXPERIMENT STATION.—NOT BOILED.

	A. Schöne-Orth Elutriation.	A-1. A. Corrected by Beaker Method.	Average of 3 Direct Beaker Elutriations.*
Above .25mm	48.82	48.82	48.82
.25-.05mm	27.36	23.72	22.37
.05-.01mm	8.63	12.08	13.70
.01- 0mm	7.36	7.55	7.20
Clay (by difference)	1.00	1.00	1.08
Loss on ignition	6.83	6.83	6 83
	100.00	100.00	100.00

The agreement between the results by direct beaker elutriation and the corrected Schöne-Orth elutriation is perhaps quite as close as could be expected. The uncorrected S.-O. elutriation materially differs from the direct beaker analysis in the 2d and 3d grades only and by five per cent. in each case.

The sample of Prairie soil whose analyses by other methods were reported last year was next examined. Fifteen grams were carefully worked with a rubber pestle to disintegrate as far as practicable all the lumps and separate the loosely adhering particles. The sample was then elutriated in the manner just described. The following figures show the results thus obtained as well as those yielded by the beaker method, as given in the report of this station for 1886, p. 157.

PRAIRIE SOIL FROM MERCER COUNTY, ILL.—NOT BOILED.

	C. Schöne-Orth Elutriation.	No. 33. Beaker Method.
Above .25mm	.76	.62
.25-.05mm	11 25	2.42
.05-.01mm	52.65	43 58
.01- 0mm	14.84	31.58
Clay	4.44	5.81
Loss on ignition	14.49	14.49
	98.43	98.50

Here the differences between the results of the two methods are such as to show positively that the Schöne process is worthless, when applied to an unboiled soil of this character. This

* Report of Conn. Ag. Exp. Station for 1886, p. 148.

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prairie earth is difficult to elutriate with a current of water because of its large content of very finely divided organic matter.

A sample of brick clay elutriated as in the above analyses gave the following results:

BRICK CLAY FROM NORTH HAVEN, CONN.*

	D. Schöne-Orth Elutriation.	No. 50. Beaker Method.
Above .25mm	1.02	1.02
.25–.05mm	3.91	.76
.05–.01mm	29.63	20.95
.01– 0mm	58.58	71.01
Loss on ignition	6 60	6.60
	99.74	100.34

We note that in this ancient drift deposit which has never been cultivated and contains no visible organic debris the Schöne elutriation totally fails to make even a rough separation of the several grades of fine matter from the unboiled soil. This failure is doubtless partly due to the fact that the current of water cannot fully disintegrate the clay, but it is also due in part to the coalescence of once separated particles as they encounter each other in the elutriating process. The coarser products of elutriation contained large numbers of fine particles, which under the microscope were seen adhering to one another in groups of from four or five up to twenty or thirty. During the analysis these flocculæ could be seen at all times in the process of formation in the elutriator, and when once formed, as Hilgard has shown, they adhere together with great persistence.

THE BERLIN–SCHÖNE METHOD.

In his original paper as printed twenty years ago in *Fresenius' Zeitschrift*, Schöne gave no definite instructions with regard to the proper duration of boiling as preliminary to the elutriating process, nor have any further communications from him on the subject appeared in the current literature.

* Not the sample analyses of which were given in report of this station for 1886.

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In the meantime his apparatus as modified by Orth has been adopted and extensively employed in the *Laboratorium für Bodenkunde*, of the Royal Prussian Geological *Landesanstalt* at Berlin. The elutriations by the Schöne apparatus that remain to be described in this paper were made as nearly as possible in accordance with the instructions that have emanated from the Berlin *Bodenlaboratorium* and are as follows:*

500 grams of the soil are sifted upon circular holes 2^{mm} diameter. Of the earth passing the sieve 30 to 100 grams are boiled in water with constant stirring for from one-half to one hour or longer, according to the character of the soil. The finer the texture of the soil the smaller the quantity taken and the longer the time of boiling. Treatment with acids or alkalies is not practiced.

The finer portion of the soil remaining suspended in the water after boiling is poured into the Schöne tube, the remaining coarse part is rinsed into the Orth tube. The clay, together with the finest sand, is collected in a separate vessel, the water in which it is suspended is evaporated off and the residue after drying in the air is weighed. The rest of the operation is carried out as previously described except that the products of elutriation are not ignited but weighed air-dry, in order that they may be further examined chemically if desired. By proceeding in this manner the following results were obtained:

SOIL FROM THE GARDEN OF THE EXPERIMENT STATION—BOILED 45 MINUTES.

Separations by the Berlin-Schöne Method.

	Air dried.	Ignited.
Above .05mm	72.63	71.76
.05–.01mm	14.17	12.53
.01–0	12.97	9.38
Loss on ignition		6.83
	99.77	99.50

* Untersuchungen des Bodens der Umgegend von Berlin, von Dr. Ernst Laufer und Dr. Felix Wahnschaffe, Berlin, 1881, pp. 14–24; also Dr. Max Fesca, Agr. Bodenuntersuchungen, p. 143. Dr. Wahnschaffe's lately published work, "Bodenuntersuchungen" had not been received when this paper went to the printer.

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For the sake of comparing the mechanical separations attainable by this procedure with those yielded by other methods, the air-dry products were ignited and again weighed and our further statements have reference chiefly to the latter.

By subtracting from the ignited portion above .05^{mm}, 49.37 per cent. the amount of this soil that remained upon a .25^{mm} sieve, the fraction between .25^{mm} and .05^{mm} is found and the separations in this analysis may be compared with those previously obtained by the Beaker Method as follows:

SOIL FROM GARDEN OF EXPERIMENT STATION.

	E. Berlin-Schöne Boiled 45 min.	Beaker Method: Boiled 23 hours av. of 4 analyses	Beaker Method: No. 29. Pestled, not boiled.	Beaker Method: Not boiled nor pestled, av. of 3 analyses.
Above 25^{mm}	49.37	47.77	48.82	48.82
.25–.05^{mm}	21.39	20.75	22.44	22.37
.05–.01^{mm}	12.53	11.18	12.55	13.70
.01–0 clay included.	9 38	13.47	9.36	8.28
Loss on ignition . . .	6.83	6.83	6.83	6.83
	99.50	100 00	100.00	100.00

Separations thus accomplished by the Berlin-Schöne method, show a very remarkable quantitative agreement with those made by the beaker method but the coincidence is more apparent than real, for on subjecting the two coarser products to beaker elutriation they were each found to contain a not inconsiderable amount of material belonging to the finer grades. The boiling for only a short time had, apparently, given the sample a composition quite different from that obtained on elutriating the unboiled soil but had not reduced it to the condition of those samples which were boiled for 23 hours. See analyses A and B, p. 256.

The following figures show the weights and per cents. of material removed by beaker elutriations from the 2d and 3d products of the foregoing analysis:

	Wt. of fractions in grams.	Wt. of substance removed.	Per cent. removed.
	Air Dried.		
.25^{mm} to .05^{mm}	22.31	2.84	12 76
.05^{mm}–.01^{mm}	14.17	1.19	8.37
	Ignited.		
.25^{mm}– 05^{mm}	21.39	2.37	11.07
.05^{mm}–.01^{mm}	12.53	.81	6.48

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The above figures supply the data for calculating a corrected Berlin-Schöne analysis which is here compared with the uncorrected analysis and with results of a beaker elutriation made directly on a sample of the same soil boiled for the same time, viz: three quarters of an hour.

SOIL FROM GARDEN OF EXPERIMENT STATION—BOILED 45 MINUTES.

	E. Berlin-Schöne Method.	E. 1. E. Corrected by the Beaker Method.	No. 49. Beaker Method.
Above .25mm	49.37	49 37	49.52
.25–.05mm	21.39	19.02	19.50
.05–.01mm	12.53	14.09	13.11
.01–.0mm	9.38	10.19	11.04
Loss on ignition	6.83	6.83	6.83
	99.50	99 50	100.00

In case of heavy loams the inability of the Berlin-Schöne method to effect even a roughly approximate separation of the several grades becomes very conspicuous, as is evident from the following figures:

CLAY LOAM, DEER RIVER, LEWIS CO., N. Y.

	Boiled One Hour.		Not Boiled.	
	Berlin-Schöne. F.	Beaker. No. 51.	Beaker. No. 30.	Beaker. No. 31.
Above .25	22.39	20.26	20.92	19.91
.25–.05	26.72	18.96	17.96	18.41
.05–.01	21.75	23.70	25.26	26.94
.01–.0	21.45	23.32	23.05	22.00
Clay		5.10*	3.55*	4.75†
Loss by ignition	7.99	7.99	7.99	7.99
	100.30	99.33	98.73	100.00

The beaker analyses, Nos. 30 and 31, were made on this soil a year ago (report of this station, 1886, p. 155‡) and are adduced for comparison with the recent analysis, No. 51. The soil here under consideration presents peculiar difficulties from the fact that it contains long-weathered fragments of clay-slate and of limestone and sandstone shales which break up on agitation, as in boiling or by pestling, into sand-

* Determined directly. † Clay and loss by difference.

‡ See this Journal, 1, 267.

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grains of various grades, and into clay, so that any means which may be employed to disintegrate the existing clay, and detach it from the coarser matters, must pulverize the latter to some extent, and thus alter the mechanical composition of the soil. In my former paper, the effects of long boiling alone, and of boiling and churn-elutriation together, in reducing the coarser and increasing the finer sediments, are set forth. Here it will be seen on comparing the beaker analyses, that boiling for one hour seems to have had little effect on the two coarser grades of this loam, but has apparently diminished the 3d grade by about 2.4 per cent., and increased the 4th and 5th by nearly the same amount. But the beaker method, for the reason above stated, cannot be expected to give such closely corresponding results on this soil as to demonstrate by a single comparison the effect of boiling for one hour.

Comparing now the two analyses made on samples of the soil similarly prepared by boiling for one hour, we notice that the first two grades in the Schöne elutriation are 9.9 per cent. higher than by the beaker process, and the three finer grades are correspondingly lower.

The last elutriation, G, attempted by this method, was on a sample of the same brick clay, whose analysis, made with the unboiled earth, has been given already. For convenience of comparison the former analysis, D, is here copied, and the results of a correction of G, by the beaker method, are also stated.

BRICK CLAY FROM NORTH HAVEN, CONN.

	Berlin-Schöne Elutriation. D. Not Boiled.	G. Boiled One Hour.	G 1. G. Corrected by Beaker Elutriation.	No. 50. Direct Beaker Elutriation.
Above .25	1.02	1 02	1.02	1.02
.25–.05	3.91	4.58	68	.76
.05–.01	29 63	29 94	22.90	20.95
.01–.0 Clay	58.58	57.14	68.08	71.01
Loss by Ignition	6.60	6.60	6.60	6.60
	99.74	99.28	99.28	100.34

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The two analyses, D and G, agree very closely, the boiling of this clay for one hour in case of G, has had but little effect over the *preliminary* pestling applied to D, in increasing the per cent. of the finest at the expense of the coarser grades.

The composition of the several sediments from the Schöne-Orth apparatus in analysis G, as found by subjecting them separately to beaker elutriation is stated in the subjoined table. The up-and-down columns under G give the Schöne-Orth elutriation products and their sub-divisions effected by the beaker process. The cross-page figures under G, when added together, give the corrected analysis G 1.

NORTH HAVEN BRICK CLAY.—BOILED ONE HOUR.

	G. Berlin-Schöne Method.					G. 1. G, Corrected by Beaker Elutriation.
	Above .05	.05–.01	.01–.0.	Loss on Ignition.	Total.	
Siftings	1.02					1.02
.25–.05	.68					.68
.05–.01	2.07	20.83				22.90
.01–.0	.89	6.13	57 14			64.16
Clay	.94	2.98				3 92
Loss by ignition				6.60		6.60
Totals G	5.60	29.94	57.14	6.60	99.28	G. 1. 99.28

SCHLÖSING'S METHOD.

According to Grandeau (Traité d'analyse des Matières Agricoles, 1887, p. 137), Schlösing's method, "has the great advantage over all the other mechanical methods yet proposed, of making known the exact content of clay and sand in the soil. The very fine sand which closely resembles clay in its physical properties, and yet in chemical character is so entirely different is not here, as in all the mechanical analyses, confounded with the clay." By this method humus and carbonates are also determined.

In the analyses thus far given in this paper, the term "clay" has been applied to that portion of the soil which remained in suspension after allowing the water in which it had been diffused, the height of which was 200^{mm}, to stand at

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rest for 24 hours (Hilgard's Conventional Method). By this means a product is obtained which consists of the greater part of the *true clay* contained in the soil, together with a considerable amount of very fine sand. The importance of separating this very fine sand from the true clay is obvious, for the chemical properties of the two are very unlike, and their influence on the physical character of the soil is different.

By *true clay* is here meant that material, mostly derived from the decomposition of feldspars and similar silicates, which is capable of uniting with a very considerable amount of water, and thus assuming a gelatinous condition in which it exerts a powerful binding action upon the particles of sand in the soil. To some extent, probably, this action is also exerted by iron and alumina hydroxides, as well as by colloid organic bodies. A relatively small amount of such clay is able to modify greatly the physical properties of a large amount of fine sand with which it is admixed, and to influence the agricultural character of the soil to a very marked degree.

Therefore, in view of the claims made for Schlösing's method, the clay obtained by his process was carefully examined for sand.

Grandeau claims for Schlösing's method more than Schlösing himself. The latter in his *Contribution a l'Etude de la Chemie Agricole, Encyclopedie Chimique*, t. x., 1885, p. 86, remarks, "We have reckoned as clay all those elements which remain in suspension in water after a repose of 24 hours. In reality these elements contain a notable proportion of very fine sand which will be deposited in the course of time. In order that the liquid may be entirely rid of this sand it is necessary to wait several weeks or even months. Such a prolongation of the analysis is evidently inadmissible. I have proposed a rest of 24 hours, for the deposition of clay.

This is a conventional time, but this convention is justified by the fact that the sediment which we call clay presents, when it has a suitable degree of humidity, a cohesion and a

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plasticity in all respects analogous to that of the natural clays."

The method as described by Grandeau is briefly as follows:

1. Thorough mechanical subdivision of the sample by working under water with the fingers.

2. Further disintegration of the sample by solution of the lime salts in weak hydrochloric acid.

3. The solution of humus in dilute caustic potash or ammonia.

4. The separation of the humus and clay from the sand by means of repeated (up to 5 or 6) subsidences of 24 hours duration.

5. Separation of the clay and humus by precipitation of the clay by potassium chloride.

6. Determination of the amount of humus by precipitating its ammonia solution by acetic acid and lead acetate.

7. Separating the sand into several grades by sifting or levigation.

The directions in Grandeau's *Traite d'analyse des matieres Agricoles*, p. 138, were carefully followed* and the results of the analyses are believed to show correctly how far the claims made by Grandeau for this method admit of vindication.

A calcareous brick clay and a prairie soil, rich in organic matter, were selected as suitable material for testing the method.

BRICK CLAY. NORTH HAVEN, CONN.

H.

Schlösing's Method.

Carbonate of lime	4.20
Sand	64.91
Clay	22.65
Humus	None
Loss on ignition	6.60
	98.36

Before weighing "sand" in the above analysis obtained by following Grandeau's directions it was further examined as

* See also Contributions a l'Etude de la Chimie Agricole Par Th. Schlösing, pp. 80-87, where a method for the "physical analysis" of soils is described, differing in various points from Grandeau's statements.

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follows: In order to remove any still adhering clay it was pestled, suspended in water and allowed to settle for 24 hours when the water and suspended soil were poured off. The sediment thus obtained was repeatedly treated in the same manner until it subsided leaving the water perfectly clear. The clay and fine sand thus removed were suspended in water and allowed to stand for several days. The supernatant liquid was poured off and the sediment thoroughly pestled and treated in the same manner as the "sand" had been. This process was repeated until the clay-water deposited no particles of sand having a diameter greater than .002^{mm}, and all the sand which had been deposited from the clay-water subsided leaving the water perfectly clear.

The sand and clay thus obtained were ignited and weighed and their sum represented the "sand" obtained according to Grandeau's directions.

This "clay" obtained according to Schlösing's method was worked over in the same manner, in order to remove from it as far as possible the fine sand which the microscope showed it to contain. From this "clay" there was thus separated 8.99 per cent. of fine sand.

The following statement of the analysis shows the result of the foregoing treatment.

		H corrected.
Carbonate of lime		4.10
Sand	Sand	65.31
	Clay	1.60
Clay	Sand	8.89
	Clay	13.66
Humus		None
Loss on ignition		6.60
		98.36

The clay thus separated still appeared to contain some very find sand (below .002^{mm} diameter) from which it could not be freed by mechanical means.

This analysis is, in most respects, not comparable with those made on the same material by other methods, but as the corrected Berlin-Schöne elutriation, G. 1, made on a sample boiled one hour, gave but 3.92 per cent. of clay, it would ap-

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pear that, of the 15.22 per cent. of clay here found, a considerable proportion must have resulted from the breaking up of concreted material by the treatment with hydrochloric acid.

With the prairie soil Schlösing's method yielded the following results.

PRAIRIE SOIL.—MERCER CO., ILL.

J.

Schlösing's Method.

Carbonate of lime	.88
Sand	82.86
Clay	7.86
Humus	1.57
Loss at 150° C	4.42
	97.59

The clay in this case contained very little sand which could be separated from it and in this respect the determination was satisfactory. The sand was elutriated by the beaker method and yielded a considerable amount of "clay" as determined according to Hilgard's conventional process. The complete elutriation of this sand may be compared with a similar elutriation of the same soil without previous treatment with acid and shows that the textural character of this soil is considerably changed by the action of dilute acids.

PRAIRIE SOIL. MERCER CO., ILL.

J. Schlösing's Method.		XIV. Beaker Method. Schlœsing's Sand. Dried at 150C.	Schlœsing's Sand. Ignited.	Original Soil. Ignited.
Carbonate of Lime,	.88			
Humus	1.57			
Loss at 150° C	4.42			
Sand	Above .25mm	.12	.10	.92
	.25–05	3 58	3.55	2.89
	.05–01	42 69	41.87	42.86
	.01–.0	01–0 23.66 / Clay* 12.81	20 47 / 10.14	31.44
Clay	7 86			7.40†
Loss on ignition,				14.49
	97 59			100 00

The figures indicate that the treatment with acid has disin-

* Determined by 24 hours subsidence. Chiefly fine sand.
† By difference.

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tegrated the particles of less than .01^{mm} diameter so that one-third of this portion would appear as clay, according to the Hilgard method of estimating clay, which we have usually employed.

As to humus it may be noted that the loss in the analysis by Schlösing's method, viz : 2.41 per cent., plus loss at 150° —4.42 per cent. plus humus found—1.57, plus carbon dioxide ($\frac{44}{56}$ of .88=).69, amounts to 9.09 per cent., while the loss ignition which represents humus, carbon dioxide (?) and water is 14.49 per cent. The 5.40 per cent. difference must evidently be, for the most part, humus which has escaped estimation by the Schlösing method, having been distributed among the sand and clay.

Schlösing, in the *Encyclopedie Chimique*, directs to calcine the sand and thus to determine as "organic *debris*" the relatively bulky vegetable matters separated by sifting or found in the coarse sand. The humus in the clay is not determined nor taken account of in the method of "physical analysis" there described.

The humus determined in analysis J, is in fact humic acid, or that part of the dead vegetable matter, which, in the soil, exists chemically united to earthy and metallic bases in forms that are highly insoluble in water but are decomposed by hydrochloric acid.

The mechanical disintegration that has resulted from the chemical action of hydrochloric acid followed by that of an alkali, in case of this soil has been due to decomposition not only of carbonates, but also and perhaps in a greater degree, to that of humates.

THE MECHANICAL DETERMINATION OF CLAY.

Schlösing's method for the separation of clay is essentially one of subsidence for 24 hours from a solution of 200 to 250^{cc} volume, but of no specified height. Hilgard's conventional method requires the same time and a height of solution of 200^{mm}.

Such methods of separation assume, first, that most of the

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sand and second, that little of the clay shall settle within the fixed time. That both of these assumptions are fallacious, the following experiments show. The "clay" obtained by 24 hours subsidence from 30 grams of brick clay was suspended in four liters of distilled water and allowed to settle out completely, which required several days. The water was then decanted off so as to remove all soluble matters, the jar again filled with distilled water and the clay and fine sand allowed to settle again for several days. The upper three-quarters of the liquid were then decanted and made up to a volume of four liters, and this was allowed to stand several days when a considerable sediment had formed. A decantation was again made as before. The operations were repeated until the clay water had been so far freed from the clay as to become opalescent; then it first ceased to deposit any appreciable sediment. A microscopic examination of the several sediments thus collected showed them all to contain particles of sand. It appears, therefore, that only after the liquid containing the clay has become opalescent does it cease to deposit fine particles of sand as well as clay.

Furthermore, the character of the true clay itself is so changed under certain conditions that it loses the property of remaining in prolonged suspension in water.

A sample of clay which had been freed from particles of sand exceeding $.005^{mm}$ diameter was suspended in water and precipitated from it by freezing. It was then washed by decantation with alcohol and dried in the air. A portion of this clay was shaken up with water and allowed to stand a few hours, during which time the greater part of it had settled. After decanting off the water and suspended clay and repeating this process a few times a very considerable part of the clay was left which would subside completely through 100^{mm} in a few hours. After standing under water for several months, only a small part of the clay had regained the quality of prolonged suspension. It was found, however, that if this clay were pestled this quality of prolonged suspension was restored to it to a very considerable degree.

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It is evident, therefore, that conventional methods depending on simple subsidence can give no accurate results because the very varying amounts of finest sand and clay in different soils will yield very variable mixtures of the two when subjected to any simple course of treatment by elutriation and subsidence.

The method of persistent pestling and repeated subsidences and decantations continued until no further separation can be effected, although extremely tedious, is the only one which has as yet yielded even approximately good separations on any of the clayey soils I have hitherto examined.

A single subsidence of the clay water for 24 hours will free it from all particles of sand having a diameter greater than $.005^{mm}$, but in many cases a considerable amount of finer sand will remain in suspension for many hours or days.

On the other hand, the sediment formed during the twenty-four hours subsidence will not be free from clay, as may be easily seen by suspending it in water a second time and allowing it to stand again for twenty-four hours. Both Hilgard and Schlösing direct attention to these defects, but assume that they do not usually influence the results to a sufficient extent to deprive them of value. In many cases this is undoubtedly true, as for example, in such soils as that from the Garden of the Experiment Station in which there is but little clay and fine sand, but in soils of the opposite character as in the North Haven brick clay where exact separatious are most desirable, a very considerable error is thus inevitably encountered.

EFFECT OF BOILING ON THE TEXTURE OF CLAYEY SOILS.

Most investigators who have worked upon mechanical soil-analysis advise boiling with water in order to detach "clay" and "sand" from each other and make good separation of the several mechanical elements practicable or possible. In general, however, the instructions as to the time and manner of boiling are rather indefinite, and no proper research as to the effects of this treatment has been undertaken.

The practice of Prof. Hilgard, to boil 24 hours or even

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longer in case of adhesive clays, would appear to be objectionable in view of the dehydration and change of physical properties known to occur in case of many hydroxides, especially those of iron and aluminum, which occur or may occur in the soil. It is a familiar fact to the chemical student that the hydroxides above named and many other amorphous substances when precipitated from cold solutions are more bulky and less easily washed upon a filter than when thrown down hot. It is also well known that their properties are considerably changed by warming or boiling with water, and St. Gilles,* Davies† and Rodman‡ have shown that heating with water to boiling for some hours or days gradually converts the bulky brown-red ferric hydroxide, which when precipitated cold and air-dried for 18 days Carnelley and Walker§ found to contain 38 per cent. of water, into a much denser bright-red substance containing but two per cent. of water. St. Gilles has also observed the partial dehydration of aluminum hydroxide (from $Al_2O_3,5H_2O$ to $Al_2O_3,2H_2O$) by prolonged boiling.

The hydrates of silica and the highly hydrated silicates are most probably affected in a similar manner, and if such be the case, boiling would evidently change the constitution of clay in a very essential degree.

The following experiments were undertaken to throw light upon this question:

10 grams of North Haven Brick Clay were boiled continuously for nine days in a glass flask of 1 liter capacity, with about 700 c. c. of distilled water and reflux condenser.

15 grams were boiled in the same manner for eight and one half days. When the boiling was concluded the soil was found to have assumed a granular condition, the clay and fine sand being collected into a mass of small grains resembling coarse sand which settled rapidly. One portion thus boiled was elutriated by the Beaker method, the other by Hilgard's. The pestle was not used on either of those portions as it was

* J. prakt. Chem., lxvi, 141.
† J. Chem. Soc. [2], iv, 66.
‡ Am. J. Sci., xliv, 1867, p. 222.
§ J. Chem. Soc., Jan., 1888, p. 76.

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desired to determine simply the effect of prolonged boiling. The separations thus accomplished are here compared with the elutriations of the same soil boiled 23 hours and of the pestled but unboiled soil.

BRICK CLAY, NORTH HAVEN.

Effect of Long Boiling (in glass).

	Hilgard Elutriation.		Beaker Elutriation.	
	Not pestled			Pestled.
	Boiled 23 hrs. XII.	Boiled 9 days. XVI.	Boiled 8¼ days. No. 40.	Not boiled. No. 27.
Sifted	3.36	3.24	3.63	3.49
.25–.05	1.21	1.11	1.91	1.29
.05–.01	28.27	33.04	33.61	27.02
01–.0	56.29	48.85	54.78	52.21
Clay	4.92	3 05	1.97	10.15
Loss on ignition	5.95	5.95	5 95	5 95
	100.00	95.24	101.85	100.11

Here it is observed that the 8–9 day's boiling diminished the clay as determined by Hilgard's conventional method by 7–8 per cent., increasing the "dust" by 2–3 per cent. and the "silt" by about 6 per cent.

Under the microscope small, rounded, opaque, brown granules were seen in large numbers, which when pressed under the cover-glass broke up into a multitude of very fine particles.

Unfortunately the sample was exhausted by these analyses and the experiment could not be repeated so as to correct the considerable error indicated by the loss in XVI.

From these experiments it would appear to be conclusively proved that too long boiling prec.pitates clay and thereby defeats the very object of the operation.

In these experiments the time of boiling was prolonged in order to bring out unmistakably the effects of this operation. If ebullition for 8 or 9 days reduces "clay" from 10 to 2–3 per cent., increasing the .05–01 ^{mm} grades by 6 per cent., it is evident that boiling for one day or a shorter time becomes a questionable treatment. In the analyses made by the use of Hilgard's churn elutriator, published in my former paper, it is easy to trace the effect of boiling. This very Brick Clay

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boiled for 23 hours is shown by analysis XII above quoted, either to have come short of sufficient disintegration in the .05–0 sediments, or if sufficiently disintegrated, to have suffered subsequent precipitation of half of the clay with those sediments.

The comparative analyses of Prairie Soil given in my former paper lead to the same alternative. The Hilgard elutriation, after 23 hours boiling, XIV (Report of this Station for 1886, p. 157) yielded less of clay by 2 per cent., less of .01–0^{mm} by nearly 5 per cent., and more of the two coarser grades by 7 per cent. than the Beaker elutriation on unboiled soil.

Whether this precipitation on boiling is simply due to dehydration by heat or is partly or wholly attributable to the action of salts extracted from the clay or from the glass of the vessel, further experiments in metallic vessels, which are already in progress, may decide.

When the clay has once been converted into the "granular" condition considerable difficulty is experienced in restoring it to the state in which it is capable of prolonged suspension in water.

The results of the studies herewith reported may be summed up as follows:

1. The Berlin-Schöne method of elutriation gives fairly correct separations with sandy soils containing little clay or matters finer than .01^{mm}, but on fine-textured soils, as loams rich in humus and clays, it gives results which are grossly inaccurate, the error on single grades amounting to 8–14 per cent.

2. In respect to rapidity, economy of time and ease of operating, the Schöne elutriation has no advantage over the Beaker method.

3. Schlösing's method on its mechanical side makes no satisfactory separations, and the chemical treatment it employs is liable seriously to alter the texture of the soil.

4. The determination of "clay" by a single subsidence from any conventional volume or depth of water, or for anv

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conventional time, is not a process certain to effect even a roughly approximate separation of the finest quartz grains from true clay.

5. Boiling with water must be rejected as a treatment preliminary to mechanical analysis, because it not only abrades and reduces the coarser sediments, but dehydrates and coagulates the true clay and thus essentially alters the texture and grain of the soil.

In a paper "On the Methods of Mechanical Soil Analysis," published in the "Proceedings of the Eighth Annual Meeting of the Society for the Promotion of Agricultural Science, 1887, pp. 48–50," Prof. E. W. Hilgard states his objections to "the subsidence method or 'beaker elutriation,'" and explains the reasons which formerly induced him "to reject this same method." Prof. Hilgard further says: "After obtaining an insight into the grave difficulties involved in the hydraulic process my first thought was to avoid them by using the obvious and simple method of subsidence, and I thus went very fully over the ground covered by Dr. Osborne's work," and again, "So far the only difference between Dr. Osborne's plan and mine is that he proposes to treat, also, the larger sized sediments ($>.28^{mm}$ hyd. value) by the subsidence method."

But Prof. Hilgard has overlooked the fact that the older "subsidence methods" differ essentially from the process which I have proposed to distinguish as "beaker-elutriation" in one very important and characteristic particular.

Prof. Hilgard says that his objection to the "subsidence method" is "simply that life seems to me too short to be occupied in painfully watching the second-hand of the watch up to the decisive moment when a short paroxysm of precipitate activity ensues, to be again succeeded by a period of enforced idleness and patience-trying watchfulness."

In my first paper (Report of this Station for 1886, p. 142), I stated nearly at the outset that "it shortly became evident that nothing is to be gained by limiting sedimentation arbitrarily to any particular intervals of time and space," and I would repeat that my process does not, as Prof. Hilgard appears to suppose, require any "close observance of the times corresponding to grain sizes," but that the eye and the micrometer alone decide the results of separations and indicate the times and the number of the subsidences, which are simply repeated until a desired result is attained and all with as much freedom to the operator as is permissible in carrying on hydraulic elutriation, or the ordinary work of the laboratory. In fact if I am able to judge impartially, the actual consumption of time and nerve in hydraulic elutriation, including the preliminary boiling, the handling of large volumes of distilled water, and of clay-water, and the use and care of delicate apparatus, is no less than in beaker elutriation.

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BECHI'S TEST FOR COTTON SEED OIL.

By H. W. Wiley.

The rapid increase of the use of cotton seed oil as a substitute for olive oil, as a constituent of margarine butters, and as an adulterant of lard has excited a lively interest in the methods for detecting this substance in mixtures. Of the many recent qualitative tests which have been proposed, none seems to have so much value as the prodecure described by Bechi.*

I have lately given this method a careful examination and with results so favorable as to induce me to make them public.

The solutions used have been of two kinds—viz. : (a) one-fifteenth to one-tenth gramme of $Ag\ NO_3$ in 200 c. c. of 95° alcohol and 20 c. c. ether.

Of this solution 10 c. c. should be taken for each test.

(b) One gramme $Ag\ NO_3$ in 200 c. c. of equal parts of alcohol and ether. Of this solution 1 c. c. was used. The mixture of 85 parts of amyl alcohol and 15 parts of rape seed oil was the same in both cases ; 10 c. c. of the mixture being used in each test. The method of making the test has also been changed. I use a porcelain dish 8 to 10 cm. in diameter. The reagents with the oil (10 c. c.) are thoroughly mixed by shaking in a test tube and then poured into the dish and placed on a steam bath. The contents of the dish are occasionally stirred and the heating is continued for 20 minutes. The deposition of silver on the dish is easily seen and the resulting colors show more clearly on the white porcelain.

Solution (b) acts more promptly than (a) but the results with (a) are more satisfactory.

The order of the phenomena will be found to be as follows :

For pure Cotton Seed Oils.—In from 2 minutes to 3 minutes the mixture turns red. In 5 to 10 minutes the red color becomes so brown as to appear black, in thick layers. At the of the test metallic silver is deposited on the sides of the dish varying in color from bluish black to reddish purple. The liquid

*See this Journal, 1, 449 ; 2, 199.

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carries also particles of reduced silver and has a decided greenish tint.

With lards containing more than 20 per cent. of cotton seed oil the phenomena observed above are repeated, but not so promptly.

Even with very small percentages of cotton seed oil, the characteristic reactions are given.

Animal fats give no color, under similar treatment, or at most a faint red after 20 minutes.

Of vegetable oils I have examined rape seed, olive, peanut and linseed. These act with the reagent like the animal fats.

One hundred samples of lard, and 25 samples of cotton seed oil have been examined by Bechi's test. In no case, where cotton seed oil has been present, has the test failed in detecting it.

Of the 100 samples of lard examined 74 were found to be adulterated with cotton seed oil.

SOME PECULIAR REACTIONS.

The reaction with crude cotton seed oil is not as sharp as with the refined oil. The deep red color of the sample seems to obscure the final color reactions.

Linseed oil gave a reddish color but no reduction of silver. In three samples of lard made by us from the leaf, guts and head respectively of the same hog—the reagent acted in the same way. There was a slightly greater coloration with the head and gut lard than with the leaf.

In samples of "Prime steam lard" passed by the Chicago Board of Trade and made from the trimmings of the whole animal not presumably including the leaf, the reagent gave after 20 minutes a slight brownish red color, but no appreciable reduction.

In the whole number of examinations made there were three or four cases in which the results appeared doubtful. A slight reduction of the silver was observed and a color approaching a brown-black, but not with sufficient positiveness to prove the presence of cotton seed oil. These I have included under the adulterated samples.

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In general it may be said that any degree of adulteration of lard with cotton seed oil which would prove commercially profitable is at once detected with certainty by Bechi's test.

On the other hand very impure lards containing no cotton seed will give color reactions and a trace of reduction of metallic silver with Bechi's reagents similar but not identical with a trace of cotton seed oil.

The reaction is undoubtedly the most valuable single test for cotton seed oil which has been proposed.

It remains to be seen what reactions lard which is made from swine fattened on mast or cotton seed meal will give with these reagents. The nature of the reducing agent has not yet been determined. It has been suggested that it is an aldehyde. It appears to withstand saponification and Milliau has lately in *Comptes rendus* proposed to use the test on the free fatty acids of cotton seed oil.

REFRACTIVE INDEX OF OILS.

By H. W. Wiley.

In 1874 Prof. Abbe of Jena published a description of his apparatus for measuring the refractive index of oils. His brochure bore the title—"Neue Apparate zur Bestimmung des Brechungs und Zerstreuungsvermögen Fester und Flüssiger Körper," published by Mauke in Jena.

Lenz[1], Strohmer[2] and Skalweit[3] have used this instrument in determining the percentages of glycerine in aqueous solution.

Müller[4] and Skalweit[5] have also called attention to the value of this instrument in the examination of butters.

1. Ztschr. anal. Chem. **19**, 302.
2. Monatshefte für Chem. **5**, 61.
3. Rep. anal. Chem. **5**, 18.
4. Archiv. d. Pharm. 1886, p. 210.
5. Rep. anal. Chem. 1886, p. 181.

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With one of the newest forms of Abbe's instrument I have lately undertaken a series of investigations of the refractive index of oils and of fats fusible below 60° C. This investigation has now been carried far enough to permit the publication of some of the results obtained.

I have so far examined the refractive index of cottou seed, lard, peanut, rape seed and olive oils and of butter fat and lard.

The principal object of my investigation so far has been to determine the effect of temperature on the refractive index. For pure water the change in refractive index is only .00008 for each 1° C. After many futile attempts to secure a reasonably constant temperature, I have succeeded in determining the refractive index of many oils at temperatures varying from 18° to 57°.

For very low temperatures I have resorted to the open air, on calm, cloudy mornings when the temperature is but little above the freezing point. For intermediate temperatures from 15° to 30°, the various rooms of the laboratory have afforded satisfactory facilities. For the high temperatures I have most successfully used the hot rooms of the Turkish bath.

A delicate thermometer, made by Geissler's successor in Bonn, reading to fifths of a degree shows the temperature at which the reading is made.

In order that the oils might quickly come to the temperature of the observation room, I have adopted, after the trial of many others, the following holder. A small glass tube is drawn out into a capillary tube and bent in the form of a U. The one arm which is the natural size of the tube serves to hold the oil, which rises in the other arm (the small tube) and is conveniently dropped on the observation prism by means of bending the end of the tube outwards at right angles with the arm, forming a spout.

When all is ready for work, the instrument and case holding the samples are exposed for a sufficient time to the temperature at which the readings are to be made. When instrument and samples have become of the same temperature as

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the surrounding air, the readings may be commenced. When there is any tendency to change in temperature, the sample should be left for some minutes in the prism before the reading is made.

For the various samples of oil three separate readings have been made at different temperatures and the results graphically entered on this cross section paper.*

It is at once evident that within the limits given the line representing the change in refractive power is straight. The variation in the refractive index therefore is constant for equal increments or decrements of temperature.

For butter fats two sets of readings have been made. It is of course obvious that such fats cannot be worked much below 30°.

Following are the numbers obtained for butter fats :

No.	*T°.*	*Index.*	
5636	32.	1.4535	
	54.6	1.4497	
Rate for each degree			.000169
5637	31.9	1.4535	
	56.2	1.4495	
Rate for each degree			.000165
5638	31.8	1.4530	
	55.0	1.4485	
Rate for each degree			.000194
5639	30.8	1.4530	
	54.8	1.4495	
Rate for each degree			.000146
5640	32.3	1.4530	
	55.8	1.4495	
Rate for each degree			.000153
5641	32.2	1.4535	
	55.4	1.4888	
Rate for each degree			.000203
5642	32.2	1.4540	
	56.6	1.4495	

*Shown at the March (1888) meeting of the Washington Chem. Soc.

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Rate for each degree			.000186
5643	32.4	1.4540	
	54.8	1.4505	
Rate for each degree			.000157
5644	32.2	1.4536	
	55.0	1.4500	
Rate for each degree			.000158
5645	31.8	1.4530	
	56.2	1.4490	
Rate for each degree			.000164
5370	31.6	1.4540	
	56.8	1.4493	
Rate for each degree			.000186
5371	31.8	1.4528	
	56.2	1.4485	
Rate for each degree			.000176

Mean rate of variation in the twelve samples for each degree of temperature 000171

With this factor the refractive index for butter can be calculated from the observed temperature to any standard of comparison.

COTTON SEED OIL.

No.	*T°.*	*Index.*	
5554	1.9	1.4755	
	22.5	1.4698	
	56.2	1.4598	
Rate for each degree			.000288
5555	1.8	1.4758	
	22.5	1.4690	
	56.6	1.4585	
Rate for each degree			.000316
5582	1.8	1.4750	
	22.8	1.4695	
	57.2	1.4592	
Rate for each degree			.000285

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5583	2.0	1.4745	
	22.8	1.4695	
	56.2	1.4593	
Rate for each degree			.000277
5615	1.8	1.4745	
	15.6	1.4698	
	56.4	1.4595	
Rate for each degree			.000273
Mean rate of variation for the five samples			.000288

LARD OIL.

5621	2.0	1.4702	
	22.8	1.4650	
	57.0	1.4548	
Rate for each degree			.000288

OLIVE OIL.

5623	1.8	1.4705	
	15.5	1.4667	
	57.2	1.4560	
Rate for each degree			.000260
5624	1.5	1.4707	
	15.7	1.4666	
	57.0	1.4560	
Rate for each degree			.000260

LINSEED OIL.

	2.0	1.4900	
	22.0	1.4835	
	56.4	1.4760	
Rate for each degree			.000258

It is seen by the above that it will be easy to determine for any given oil the rate of variation in the index of refraction as influenced by temperature and thus be able to calculate to a standard temperature from any given temperature of observation.

It is further noticed that the rates of variation are very different for different oils, being very much less, for instance, in

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butter fats than in cotton seed oil. It is also noticed that the index of refraction is higher in cotton seed oil than in olive oil, while in linseed oil the very high index of refraction would enable the analyst to detect at once, by means of the refractometer, an admixture with any of the oils mentioned above.

LIST OF ELEMENTARY SUBSTANCES ANNOUNCED FROM 1877 TO 1887.

COMPILED BY H. CARRINGTON BOLTON.

Date	*Name.*	*Source.*	*Authority.*
1877	Neptunium	Columbite	Hermann.
	Lavcesium	Pyrite	Prat.
	Mosandrum	Samarskite	J. L. Smith.
	Davyum	Platinum ores	Sergius Kern.
1878	"New earths"	Unnamed mineral	Gerland.
	"X"	Gadolinite	Soret.
	Philippium	Samarskite	Delafontaine.
	Decipium	Samarskite	Delafontaine.
	Ytterbium	Gadolinite	Marignac.
1879	Scandium	Gadolinite	Nilson.
	Norwegium	Gersdorffite	Dahll.
	Uralium	Platinum	Guyard.
	Samarium	Samarskite	Lecoq de Boisbaudran.
	Barcenium	(Misapprehension)	Wagner's Jahresbericht
	Thulium	Gadolinite	Cleve.
	Holmium	Gadolinite	Cleve.
	Columbium	Samarskite	J. L. Smith.
	Rogerium	Samarskite	J. L. Smith.
	Vesbium	Lava	Scacchi.
1880	Comesium		Kaemmerer.
	Yα and Yβ	Gadolinite	Marignac.
1881	Actinium	Zinc ores	Phipson.
1882	Didymiumβ	Gadolinite	Cleve.
1883	Nameless	Platinum ore	Th. Wilm
1884	Idunium	Vanadium ore	Websky
1885	Neodymium	Didymium	Von Welsbach.
	Praseodymium	"	"
	Zα	"	Lecoq de Boisbaudran.
	Zβ	"	"
1886	Zγ	Terbia, &c	"
	Germanium	Argyrodite	Winkler.
	Dysprosium	Holmium	Lecoq de Boisbaudran.
	Austrium	Orthite	Linnemann.
	Dα	Didymium	Crookes.
	Sβ	Samarskite	"
	Gα	Gadolinite	"
	Gγ	"	"
	Gδ	"	"
	Gϵ	"	"

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Date.	Name.	Source.	Authority.
1886	Sδ	Samarskite	Crookes.
	Gζ	Gadolinite	"
	Gη	"	"
	Polymnestum	Glacial debris	Pringle.
	Nameless (1)	" "	"
	Erebodium	" "	"
	Nameless (2)	" "	"
	Gadenium	" "	"
	Hesperisium	" "	"
	Gadolinium=Yα		Marignac.
1887	Erα	Erbia	Krüss and Nilson.
	Erβ	"	"
	Tmα	Thulium	"
	Tmβ	"	"
	Smα	Samarium	"
	Smβ	"	"
	Xα to Xη (7)	Soret's X	"
	Diα to Diκ (10)	Didymia	"

DETERMINATION OF PHOSPHORUS IN IRON AND STEEL.*

By Porter W. Shimer, M. E.

The solution used in the following method for phosphorus determination is the filtrate obtained in the nitric and sulphuric acid method for the determination of silicon (Trans. Am. Inst. Min. Eng., Vol. VII, p. 346). This filtrate, being easily and quickly obtained, and always quite free from silica, is a desirable one for phosphorus precipitation. In order, however, to get all the phosphorus in a precipitable form, the solution must be made under conditions more strongly oxidizing than simple solution in boiling nitric acid. In a solution thus made I have found that the presence of a moderate amount of free sulphuric acid does not prevent complete precipitation of the phosphorus.

The method in detail is as follows: Dissolve 1 grm. of iron in 20 c. c. HNO_3, sp. gr. 1.20. Add to the boiling solution 10 c. c. potassium permanganate solution (20 grms. to 1000 c. c. water, filtered), 2½ c. c. at a time. After a few minutes, when the permanganate is decomposed, leaving a heavy precipitate of MnO_2, add 5 c. c. HCl, 1.12 sp. gr. When the effervescence due to the escape of chlorine has ceased, add a

*Read at the Birmingham Meeting, Amer. Inst. Min. Eng., May, 1888.

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mixture of 5 c. c. strong H_2SO_4 and 5 c. c. water. Remove the watch-glass and evaporate till fumes of SO_3 begin to come off. Allow to cool and add 5 c. c. HNO_3, 1.20 sp. gr. and enough water to dissolve the residue. Boil till all iron salts are dissolved and filter, washing with water alone. For silicon the residue should be washed a few times with HCl and water to remove possible traces of iron, but these washings should not be added to the phosphorus solution. The latter solution (which need not be concentrated by evaporation when unnecessary excess of wash-water is avoided) is heated to 80°C., and 50 c. c. of ammonium molybdate solution is added (5 grms. MoO_3, 20 c. c. NH_4HO sp. gr. 0.96 and 30 c. c. HNO_3, sp. gr. 1.20). Heat to 60° C. till the supernatant liquid is clear. When the solution is not too dilute precipitation is complete in less than one hour. The yellow precipitate is filtered off; washed with acid ammonium nitrate solution; dissolved in ammonia and precipitated by magnesia mixture. The ammoniacal solution is more generally colorless and clear than that obtained by the usual method. In case the ammoniacal solution of the yellow precipitate is not perfectly clear and colorless it is my custom to dissolve in HCl whatever gelatinous residue there may be upon the paper, allowing the acid solution to drop into the ammoniacal filtrate below until it becomes acid, thus throwing down the yellow precipitate. Add a slight excess of ammonia, and boil for a few minutes. Filter off the precipitate and dissolve it on the paper in a few drops of HNO_3 and add ammonium molybdate solution. Add the ammoniacal solution of the precipitate thus obtained to the main solution. The latter is then precipitated by magnesia mixture in the usual manner.

When the solution of the iron is made as above no phosphorus can escape complete oxidation, for it is subjected to the following oxidizing agencies: Solution in boiling HNO_3; action of potassium permanganate solution; action of chlorine given off by the reaction of HCl on MnO_2; action of chlorine given off by mixture of strong HCl and HNO_3; evaporation and heating till fumes of SO_3 appear; solution of residue in

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water and HNO_3. These agencies are also desirable for the oxidation of silicon, for there is reason to suspect that this element is not easily oxidized in some irons.

The following are some comparative results obtained. The standard method is the usual one of solution in HNO_3; evaporation to hard dryness; solution of the residue in HCl; replacement of HCl by HNO_3, precipitation by molybdate solution, and final precipitation by magnesia mixture.

	Standard Method. Phos. per cent.	*Method above Described.* Phos. per cent.
A	1.75	1.74 1.76 1.76
B	3.623 3.641	3.639 3.637
C	0.560	0.558
D	0.394	0.397
E	0.582	0.588
F	0.073	0.072 0.074
G	0.749	0.749

In the case of the Bessemer iron 5 grms. iron were taken and 8 c. c. H_2SO_4 instead of 5 c. c. Sample "B" is a white iron containing 2.27 per cent. combined carbon and 0.08 per per cent. graphite. In sample "G," Mr. Lee S. Clymer, chemist Durham Iron Works, obtained, by the usual acetate method, 0.743 per cent., and, by applying the acetate method to the filtrate from the silicon as obtained above, he obtained 0.743, 0.740 per cent. phosphorus.

The exactness with which the kind and amount of free acid can be controlled in this solution for molybdate precipitation, and the comparative purity of the yellow precipitate in case of titanic irons, would probably make it well adapted either for weighing directly or for solution, reduction and titration according to the method described by F. A. Emmerton, Vol. XV, Trans. Am. Inst. Min. Eng., p. 93.

N. H. Muhlenberg and Thomas M. Drown (Trans. Am.

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Inst. Min. Eng., Vol. X, p. 85, 329) evaporate the solution of the iron in nitric and sulphuric acids to dryness, and heat till SO_3 fumes cease coming off. The phosphorus results obtained are accurate, but the silicon results are high. It is unnecessary however to drive off dense volumes of these irritating fumes, for complete precipitation depends, not upon absence of free sulphuric acid, but upon complete oxidation of the phosphorus, and of the carbon compounds resulting from solution of combined carbon in nitric acid. Moreover a certain amount of free sulphuric acid is necessary for a good silicon determination.

It may be interesting to add the results of a few experiments with a molybdate solution containing sulphuric acid instead of nitric acid. The solution for phosphorus precipitation was made as above with the exception that the residue on evaporation with H_2SO_4 was dissolved in water alone instead of water and HNO_3. This solution was heated to 80° C. and precipitated with a molybdate solution made by dissolving 5 grms. molybdic acid in 20 c. c. NH_4HO, sp. gr. 0.96 and adding 30 c. c. dilute H_2SO_4 (1 part acid to 4 parts water). After heating for one half hour to 60° C. precipitation was complete. The results were as follows:

	By standard method.	*By use of Sulphuric Molybdate Solution.*
	Phos. per cent.	*Phos. per cent.*
A	1.75	1.75
B	3.63	3.64

It will be noticed that in these precipitations sulphuric acid and ammonium sulphate have completely taken the place of nitric acid and ammonium nitrate. Another experiment on the iron marked "B," in which however 25 c. c. more free sulphuric acid was present, gave only 3.09 per cent. phosphorus, showing that a too large excess of free sulphuric acid prevents complete precipitation just like too large an excess of free nitric acid.

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COBALT SOLUTION AS AN INDICATOR IN FERRIC IRON DETERMINATIONS.

By Alonzo C. Campbell.

In the January number of this journal* I discussed some experimental operations in the use of cobaltous chloride as a delicate indicator in the volumetric determination of ferric iron by the use of stannous chloride.

I beg leave now to offer further results in the same line of research.

Stannous chloride has always been acceptable as a reagent, but on account of its tendency to perchloridization by the ingress of atmospheric oxygen it has been to say the least very troublesome. It is further objectionable on account of the necessity of diluting to such an extent to reduce the possible error. Again the dilute standard needs to be added in such quantity that the delicacy of the indicator is in great degree destroyed, and the time of the operation is so prolonged that it favors atmospheric oxidation. There are many other objectionable features attending the use of this reagent, and altogether it would be more acceptable if it were more manageable.

I will propose a method which appears to satisfy the demands and will detail the several steps so far as it has been perfected.

Secure a large sheet of bright, pure tin foil, cut it into long strips of variable sizes so that the weights may be about .100 to .500. It is necessary to determine the reducing power of the foil, and as a first approach the terms of the reaction may serve $SnCl_2+Fe_2Cl_6=SnCl_4+2FeCl_2$.

In accordance with this reaction 118 of metallic tin should mark the presence of 112 of metallic iron, and 1. of tin should represent .95 of iron. Then it remains to dissolve first a weight of pure wire suitable to a known weight of tin foil, say .500 of tin which would be .475 or less of iron. The wire is then dissolved in a 50 c. c. flask and perchloridized by potas-

*2, 4.

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sium chlorate and the solution reduced in volume. The tin foil is next dissolved in a flask of the same size and a few drops of cobaltous chloride added. Both flasks being now boiling hot the ferric chloride is cautiously poured into the tin solution. At first the clear blue will stand firm, but as the last remnants of ferric iron enter pure green will more strongly maintain its hold. The flask is then washed by repeated additions of small quantities of water.

It remains now to conclude from the degree of coloration (blue or green) whether ferric iron is in excess or deficient. If the blue should hold a further addition of ferric iron solution of know standard will serve to balance the reaction. This done the exact ratios of metallic tin to metallic iron is known, and if one is given the other can be determined. I found by careful approaches that 1,000 of tin equalled .924 of iron instead of .95, which was due probably to impurities of the tin.

The tin being thus standardised and a number of carefully weighed and marked strips being at hand, a couple of 50 c. c. flasks, a 10 c. c. burette, a small bottle of cobaltous chloride, and a standardised solution of ferric iron, all is ready for an actual determination in a simple and satisfactory manner.

To make the process quite clear the following determinations may serve: The ore was a ferruginous limestone. There was taken .460 of tin, 2.000 of ore, and a balance of 7.2 c. c. of standard solution of iron, such that 1 c. c. equaled .01 of metallic iron: $.460 \times .924 - .072 = .353$, which would be 17.65 per cent. metallic iron in the ore. Another ore gave .404 tin 7.8 c. c. standard in 2.00 of ore, which would give 14.5 per cent. of iron.

It is important to make an approximate guess or estimate of the percentage of iron an ore or mineral may contain, in order to make a more ready and accurate determination; and I would recommend the colorometric method. Ferric chloride in strong hydrochloric solution gives a depth of yellow proportionate to the amount of iron in a given volume, and thus a series of well chosen samples of ferric solution of known percentage would serve by comparison to form a close esti-

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mate of iron in any solution. With this precaution an approach within two or three per cent. might be made, which would require the addition of 2 or 3 c. c. of standard.

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STANNOUS BORATE AS A QUANTITATIVE COLORIMETRIC REAGENT.

BY ALONZO C. CAMPBELL.

As a further step in the improvement upon the method of ferric iron determination I have to offer stannous borate in the dry state as an invariable salt, which I think may prove superior to any reagent in use. It would not be proper to call this a volumetric method as will appear.

Place a quantity of crystals of stannous chloride in a flask to which add a little hydrochloric acid and some metallic tin. Boil till all of the stannic tin has been reduced. To this solution add sodium carbonate to slight permanent precipitation, then enough calcined borax to precipitate all of the tin, which is partially washed and then thoroughly dried at a moderate temperature.

Weigh on a watch glass a quantity of the powder for immediate use. The iron may be dissolved in a 50 c. c. flask and treated at once without filtration from silica. The cobaltous chloride being added the stannous borate remains to be added in the following manner: Use a glass rod flattened at one end and bent at right angles, much like a hoe, and of suitable size to enter the mouth of the flask. This glass hoe is held in a perpendicular position over the watch glass and by the aid of a small pointed spatula a portion of the powder is deposited upon the flattened area when it is ready to be thrust down the neck of the flask and into the ferric solution, when by stirring a few rounds the powder quickly dissolves, and as quickly performs its reducing service. Another charge is added, and another, and finally observing the precaution to add just enough to bring out the true blue. If too much has

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been added it is titrated back with a very weak standard solution of ferric iron, measuring the amount by counting the drops from a small glass tube pipette, the number of drops to the c. c. having been determined. The amount of iron thus added being deducted from the total as deduced from the known weight of stannous borate should give the weight of iron in the ore.

It will of course be understood that the stannous borate needs to be standardised by a known weight of metallic wire in solution.

This method I claim is superior in accuracy to any volumetric or gravemetric method in use, because of the small volume of the solution and the delicacy of the indicator. There need not be a greater volume than 5 or 10 c. c. in which a trace of ferric iron should cause a perceptible coloration. I have made repeated trials of this method with very slight variation of results. There is one advantage particularly in its favor—there is no stannous chloride to suffer change by extraneous oxidation, since the moment it enters into solution it exercises its full reducing effect upon the ferric iron. This reaction takes place in the cold just as thoroughly and with the same results as when heated; but heat hastens the operation somewhat. At the moment of the decomposition of the borate the resultant product in reason should act with greater avidity due to its passing atomic condition, and such appears to be the case.

To test the constancy of the borate in the open air I weighed out a quantity on a watch glass and exposed it for twelve hours or more—there was no material change of weight.

I have tried this method in the determination of nitric acid, also cupric chloride, and it works equally as well as with the ferric iron, and I am sure there is a much wider field for its application.

I would say in response to Prof. Morgan's results as published in the preceding Journal that I think his experiments are conclusive as I thought Mr. Venable's were.

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SEPARATION OF FERRIC IRON FROM COBALT, NICKEL AND MANGANESE.

By Alonzo C. Campbell.

In the separation of iron from the metals, cobalt, nickel, and manganese, advantage is taken of the disposition which iron has of being most stable in the sesqui state, while the other metals incline to the lower degree of oxidation. The much dreaded basic acetate practice is yet, I think, in vogue for the want of something better, and these four metals are so closely akin in all their reactions and chemical relations that it has been difficult to devise a means of separation that is sufficient in all particulars.

Preparatory to a description of the method which I have to offer I will mention a few reactions bearing upon the process.

Place in a 50 c. c. flask a solution of cobaltous chloride, to which add carbonate of soda to complete precipitation. To this precipitate add some crystals of chloride of lead. The cobaltous carbonate is dissolved while carbonate of lead is precipitated. Gentle warming favors the reaction. In like manner carbonate of nickel or manganese may be dissolved by lead chloride. Ferrous carbonate is likewise soluble, but ferric oxide is insoluble. Now place in the flask a solution of cobaltous chloride as before and to this add a milk of carbonate of lead holding a trace of chloride of lead so there shall be no free alkali. The cobalt is not in the least affected, and this is true also of salts of nickel, manganese and ferrous iron. But ferric iron, or probably basic ferric chloride, is precipitated completely if enough of the lead carbonate has been added. It will appear from the experiments that a perfect separation of ferric iron from the remaining metals is possible provided reasonable precaution be taken to prevent peroxidation of manganese and cobalt. There should be no nitrate present and the precipitation should be made in a flask, and gentle warming is sufficient to precipitate all the iron. This precipitation is thorough whether in dilute or concentrated solutions, and the precipitate is of a nature well suited to rapid filtration and thorough washing.

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The basic acetate precipitation which requires a dilute solution gives a voluminous flocculent or jelly-like precipitate that requires many precautions and a great length of time for finished washing, and the whole operation involves so many possible errors that the task is too often recklessly shirked.

Lead carbonate or lead oxide will precipitate a basic salt from any acid solution. Acetate of lead will also precipitate a basic salt of iron, and is superior to the acetate of soda since lead chloride is formed in the reaction which acts as a solvent to prevent the precipitation of the other metals.

After the precipitation and washing there is left on the filter all of the iron (and alumina and titanic oxide if present) together with some basic salt of lead, with the small excess of lead carbonate. In the filtrate is found all of the cobalt nickel and manganese (and ferrous iron if present) together with lead chloride.

The precipitate is treated with hot dilute sulphuric acid which dissolves all of the iron, leaving the insoluble lead sulphate on the filter. The solution of iron may be determined by the stannous borate method. The filtrate remains to be treated with hydrogen sulphide, thus precipitating the lead which is filtered from the remaining metals.

In order to determine the accuracy of this method I prepared solutions of variable proportions of nickel cobalt and iron, and after one precipitation tested the solution of iron for the other metals by the following method: Dissolve the precipitate of basic chloride of iron in hydrochloric acid, evaporate to small volume then add some scraps of tin foil and boil till the ferric iron has been entirely reduced to the colorless ferrous chloride. This done, if there is a trace of cobalt the solution will be blue. If any nickel be present the solution will be green. If both are present the color will be bluish-green or greenish-blue, depending upon the proportion of the two metals.

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THE KJELDAHL PROCESS FOR THE DETERMINATION OF NITROGEN.*

By E. Waller and H. C. Bowen.

This process was devised by Kjeldahl, of Copenhagen, for use in connection with the brewing industry. The details were first published in 1883.†

A convenient amount of the nitrogenous material (0.5 to 1 gm.) was heated in a flask with 10 c. c. concentrated sulphuric acid with addition of Nordhausen acid, or phosphoric anhydride, until the solution was nearly colorless. Pulverized potassium permanganate was then cautiously added (to complete the destruction of the organic matter), until the green color of manganic acid appeared. After cooling and diluting, an excess of caustic soda solution was added, and on distilling, the nitrogen (now in the form of ammonia) was titrated in the distillate. The acid was caused to act upon the material at a temperature just short of boiling. To prevent the otherwise inevitable bumping on distilling with the soda, a few pieces of metallic zinc were added to the retort or distilling flask.

Kjeldahl found that the process, as described, failed to give all of the nitrogen as ammonia in some compounds of the fatty and aromatic series, in some alkaloids, and in nitrates, though as regards the latter, when sugar was added, a much larger proportion (60 to 80 per cent.) of the nitrogen than was expected was found to be converted into ammonia.

The theory of the process is given by Dafert as follows:

1. The acid withdraws from the material the elements of water.

2. The action of the acid upon the organic substance also affords SO_2, which acts reducing upon the nitrogenous material.

3. Where some nitrogenous compounds partially resist this action, the permanganate added toward the close of the acid treatment breaks them up, forming ammonia.

* From School of Mines Quarterly.
† Ztschr. anal. Chem., xxii, 366.

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TREATMENT WITH ACID.

The relative proportions of concentrated sulphuric acid, Nordhausen and phosphoric anhydride, are not specified in the original paper. The proportion of Nordhausen acid used by different experimenters is from 20 to 50 per cent. Some, as Pflüger and Bohland, Kulisch, etc., use no phosphoric anhydride. Wilfarth also regards it as unnecessary when metallic oxides are used. It is noted by Kreusler and others that Nordhausen acid frequently contains nitric acid, which may consequently give untrustworthy results.

The proportion of phosphoric anhydride used is from 10 to 25 per cent. Some (as Kreusler) use phosphoric anhydride and omit the use of Nordhausen altogether, in some cases, however, using in its stead the metallic oxides recommended by Wilfarth. Wilfarth's modification consists in the addition of about 0.1 to 0.6 gm. CuO, and 0.7 gm. HgO.

This recommendation has been further modified by the suggestion to use the anhydrous sulphates of those metals, or even metallic mercury in place of the oxide. HgO, prepared by heating the nitrate, is inadmissible in any case.

Kulisch, in experimenting on wines, found the addition of CuO to afford but little advantage in point of speed, which was one of the main points claimed by Wilfarth.

Schmitz applied Wilfarth's method successfully in the analysis of coal and coke.

Ulsch found that the operation was hastened by the addition of 5 drops of a $PtCl_4$ solution containing 0.04 gm. metallic Pt per c. c. Platinum black was unsatisfactory. Adding also 0.05 gm. CuO gave still better results. He found, however, that an excess of platinic chloride might easily cause loss of nitrogen.

Adding the acid by instalments was found to be of advantage in certain researches of C. Arnold, and of Brunemann and Seyfert. About one-fourth of the whole amount of acid was first added, and the flask gently heated until frothing had materially diminished, when the remaining three-fourths were added, and the operation conducted as usual.

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It is asserted by Lenz that the size of the flask in which the operation is conducted has a material influence upon the amount of acid and of time required for effecting the decomposition. This may be the cause of the wide disagreement of different experimenters on those points.

To avoid loss by spattering, some use long, slender-necked flasks, while many others use some perforated bulb stopper arrangement in the neck of the flask. Slanting the flask also is another device. Special forms of heaters, protecting the flasks by wire gauze, or using the naked flame, etc., are details which have been differently managed by different analysts.

USE OF PERMANGANATE.

Czeczetka proposes the use of a solution of the permanganate in concentrated sulphuric acid, instead of the pulverized form. Lenz, Kulisch and some others regard the use of this reagent as a very necessary part of the operation, but C. Arnold, as well as several others omit it as useless. With these latter, Asboth agrees only partly, stating that it is necessary in the case of difficultly decomposible substances, as morphine, etc. On the other hand, Wilfarth and some others regard its use as involving possible loss of ammonia. Many of the chemists referred to quote analyses in support of their views on this point.

DISTILLATION.

Bumping is prevented by passing a current of steam through the solution, by Petri and Lehmann.

Asboth adds enough Rochelle salt to prevent any precipitation of metallic hydrates by the alkali. Wilfarth found that bumping occurred when soda was used, but not with potash. Scovell's experience is exactly the reverse. It is noted by many experimenters that the evolution of hydrogen when metallic zinc is added, causes some of the alkali to be carried into the distillate, and to obviate this, some advise interposing wire gauze, or glass beads, etc., in the neck of the distilling flask, while others use a bulbed tube above the flask. Much of the caustic soda and potash sold for laboratory use has been puri-

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fied by fusion with nitrate, and in contact with zinc this may afford enough ammonia to interfere with the correctness of the results.

When mercury or its compounds have been used in the treatment with acid (Wilfarth's process), potassium or sodium sulphide must be added, to break up the mercur-ammonium compounds. Ulsch uses ferrous sulphate for that purpose.

PRESENCE OF NITRATES.

To *remove* nitrates when present, Warrington first heats the material with ferrous sulphate and hydrochloric acid, and, after drying, proceeds as usual. Reitmair accomplishes this by heating the substance with sulphuric acid in a tin capsule, finally throwing capsule and contents into the decomposition flask. The French Association of Sugar Chemists remove the nitrates by heating for some time at 110° C. in contact with oxalic acid.

To *determine* the nitrogen in nitrates by this method, Asboth proposes the addition of about 17 gms. benzoic acid to every 0.5 of nitrate. Spencer and C. Arnold, however, did not obtain satisfactory results by this means, though the latter found it fairly good when larger amounts of benzoic acid were used. Jodblauer proposed the use of phenol sulphuric acid, followed by zinc dust, the theory being that nitrophenol is at first formed, which by the action of the zinc is converted to an amide, and by the subsequent treatment into ammonia. Stutzer and Reitmair only find this method effective after treating the material with water, and evaporating to dryness in order to distribute the nitrate through the mass in a finely divided condition. Salicylic acid, instead of phenol, has been found by Scovell to be more advantageous. He prescribes for 0.7 to 1.4 gms. of the substance, 30 c. c. sulphuric acid and 2 gms. of salicylic acid, followed by the gradual addition of 8 gms. of Zn dust, and then 2 or 3 drops of platinic chloride. After gentle heating until frothing ceases, and then more strongly for five or ten minutes, 0.7 gm. HgO is added, and the heating continued as usual.

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GENERAL.

The process commends itself in the examination of many nitrogenous substances, on the score of expense of material and of trouble; in the matter of economy of time, the statements are very diverse. It seems hardly safe as yet to claim for the process universal applicability. It has been noted, especially with azo and diazo compounds, that the treatment permits of some loss of nitrogen in the elemental state, and with some others, as those of the pyridin and chinolin group, the process seems to fail.

In using this process upon fertilizers, flour, cattle foods, and material of that nature, we have found that many of the devices recommended by other experimenters can be made unnecessary. A method found to be satisfactory is as follows:

The substance to be examined is first tested as regards its action with concentrated sulphuric acid. Then 0.5 to 1.5 gms. of the material is weighed out in a flask of 100 to 150 c. c. capacity; the flask should have preferably a short wide neck (nearly one inch in diameter). Enough concentrated sulphuric acid (usually 5 to 12 c. c.) is then added, to maintain a liquid state of the mixture on heating. If too little acid is used, a coke-like mass results, which is difficult to manage. After adding the acid, a short funnel with wide stem may be inserted in the neck. Such funnels may be easily made from glass tubing of about ⅜ inch internal caliber. The heat is applied gently until foaming ceases, when it is gradually increased. The heating is performed on a tin plate, with or without a bit of sheet asbestos under the flask. When the condition of the contents of the flask will permit it (which is usually very soon after frothing has ceased) a clay chimney is placed about the flask, to protect it from the cooling influence of the external air. *The mouth of the flask and funnel must be below the top of the protecting chimney or guard.* It may even be well to lay a clock glass across the top of the guard, leaving of course some exit for the fumes. The flame of a good Bunsen burner may be applied, to the extent of heating the supporting plate to a cherry-red. Thus

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arranged, the oxidation and simultaneous evaporation of the sulphuric acid proceeds very rapidly. The heating is kept up until the contents of the flask are reduced to about 2 c. c. Under the conditions described this will take about an hour. Ordinarily the solution is then quite colorless, at times it has a pale, reddish tint, and sometimes, though rarely, the reddish tint is deeper. In the latter case 2 to 3 c. c. of Nordhausen acid are added, and it is heated as before.

After obtaining a solution which is nearly or quite colorless, the contents of the flask are allowed to cool before adding the permanganate (in powder). After adding this reagent, gentle warming will cause it to exert its effect. Now evaporate down to about 1.5 c. c., cool, dilute with water to about 150 c. c. and transfer to an Erlenmeyer flask of about 250 c. c. capacity, having a doubly perforated stopper. Through one hole passes a bulbed exit tube leading to the condenser, through the other a stop-cock funnel tube, the end of which reaches nearly to the bottom of the flask. Through the latter a solution of caustic soda or potash is introduced, in sufficient quantity to give a decided precipitate of manganous hydrate. The distillation can then be effected without difficulty. The end of the condenser is allowed to dip into water containing a known amount of standard acid, which is titrated back as usual, after distilling off about one-half of the contents of the flask.

The principal advantages of this mode of management consist in a marked saving of time, and increased effectiveness of the sulphuric acid, thus dispensing for ordinary work, with any addition of phosphoric anhydride, metallic oxides, etc. Moreover, by driving off much of the excess of acid, and exercising reasonable care in the neutralization of the remainder, the distillation can be effected without danger from the bumping of the solution.

We have not investigated as to how far it may be possible to omit altogether the use of the permanganate, though it seems probable that in many cases it might be dispensed with.

In the table below are some of the results obtained, as com-

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pared with the Ruffle and absolute methods. The results on sodic nitrate and fertilizers containing nitrate are only given as confirmatory of the failure of the method to give trustworthy results without modification. With pure nitrate a considerable quantity of sugar was used. The Ruffle method also fails in presence of nitrates.

	Kjeldahl.	*Ruffle.*	*Absolute.*	*Theory.*
Urea	46.662	....	....	46.754
"	46.620	....	....	46.754
"	46.816	....	...	46.754
"	46.704	....	....	46.754
Impure ammonia sulphate	20.42	20.70	....	21.21
Sodic nitrate	4.49	11.64	16.6	16.47
Cotton-seed meal	6.10	6.30	6.37	
" hulls	0.448	....	...	
Fertilizer	2.72	2.42	2 74	
"	2.26	2 33	2.25	
" containing nitrate	1.18	2.00	2.40	
" "	1.93	2.36	2.44	
" "	3.44	4.06	4.51	

It may also be added that the students in the Quantitative Laboratory of the School of Mines have repeatedly obtained, by the Kjeldahl process, results on fertilizers which agree closely with those obtained by the more elaborate combustion processes.

We append references to the literature on the process, arranged alphabetically as to authors' names.

Arnold.—Arch. Pharm. (3d ser.), xxiii, 177; xxiv, 785. Chem. Centralblatt, 3d ser., xvii, 337. Ztschr. anal. Chem., xxv, 454. Rep. anal. Chem., iv, 97.

Armsby.—Am. Chem. J., viii, 323.

von Asboth.—Chem. Centralblatt, 3d ser., xvii, 161.

Balcke.—Wochenschrift f. Brauerei, i, No. 11.

Bohland.—Arch. f. gesammt. Physiol, xxxv, 454; xxxvi, 102; and xxxvii, 423.

Bosshard.—Zeitschr. f. Physiol. Chem., ix, 63. Ztschr. anal. Chem., xxiv, 199.

Brunemann.—Chem. Ztg., viii, 1820.

Czeczetka.—Monatsh. Chem., vi, 63.

Dafert.—Sitzungsber. Niedershein Gesell., 1884, 203. Landwirths. Versuchs Stat., xxxiv, 311.

Farrington.—U. S. Dept. Agric. Bulletin, No. 16.

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Hannin.—Ztschr. anal. Chem., xxv, 155.
Heffter.—Chem. Ztg , viii, 432.
Hollrung.—Chem. Ztg., viii, 432.
Jodblauer.—Chem. Centralblatt (3d ser.), xvii, 433.
Kjeldahl.—Ztschr. anal. Chem., xxii, 366
Kreusler.—Ztschr. anal. Chem., xxiv, 393. Landwirths. Versuchs Stat., xxxi, 209.
Kulisch.—Ztschr. anal. Chem., xxv, 149.
Lehmann.—Ztschr. anal. Chem., xxiv, 388. Zeits. Physiol. Chem., viii, 200.
Lenz.—Ztschr. anal. Chem., xxvi, 590.
Märcker.—Zeit. f. Spiritus Ind., viii, 223. Wochenschr. f. Brau , 1886, 190.
Morgen.—Chem. Ztg., viii, 432.
Neal.—Report of N. J. Agric. Exper. Station, 1886.
Petri.—Zeits. f. Physiol. Chem., viii, 200.
Pfeiffer.—Ztschr. anal. Chem., xxiv, 388.
Pfluger.—Arch. f. gesammt. Physiol., xxxvi, 102.
Reitmair—Rep. Anal. Chem., v, 232 and 262 ; vii, 4.
Rindall.—Ztschr. anal. Chem , xxv, 155.
Reinke.—Wochenschr. f. Brau., 1885, 191.
Rube.—Ztschr. anal Chem., xxiii, 43.
Ross.—Chem. News, lv, 151.
Schmitz.—Ztschr. anal. Chem., xxv, 314.
Scovell.—U. S. Dept. Agric. Bulletin, No. 16.
Seyfert.—Chem. Ztg., viii, 1820.
Short.—Am. Chem. J., viii, 323.
Spencer.—Chem. News, lv, 20.
Stebbins.—J. Am. Chem. Soc. vii, 108.
Stutzer.—Rep. Anal. Chem., v, 232, and vii, 4.
Ulsch.—Chem. Centr. (3), xviii, 284. Zeits. gesammt. Brau , 1886, 81 ; 1887, 3.
Warrington.—Chem. News, lii, 162.
Wilfarth.—Chem. Centr. (3d ser.), xvi, 17 and 113.
Wilkinson.—Chem. News, lv, 151.
Yardley.—Chem. News, lii, 220.

Abstracts of many of these papers may be found in

Chem. Soc., xlvi, 364 ; xlviii, 430, 688, 837, 930, 1261 ; l, 179, 282, 648, 652, 834, 1071 ; lii, 78, 298, 863.
Chem. News, xlviii, 101 ; l, 58 ; li, 285 ; lii ; 107 ; lv, 249 ; lvii, 64.
Ztschr. anal. Chem., xxiii, 596 ; xxiv, 299, 453, 635 ; xxv, 252, 280, 426, 575 ; xxvi, 92, 249, 646 ; xxvii, 73.

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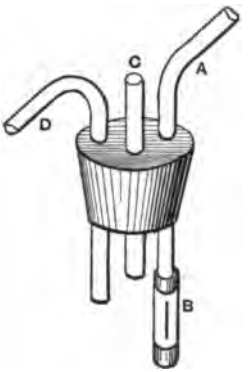
WASH BOTTLE FOR AMMONIA.

By F. M. Haldeman.

Having been annoyed by fumes entering my mouth when using the ordinary wash bottle for ammonia and hot acids, I contrived the following arrangement which does away with that trouble. The blowing tube A is furnished with a valve B made out of a slit rubber tube. A third tube passes through the cork near the edge so that it can be covered with the thumb. By keeping C closed and blowing through A the liquid will run in a good strong stream as long as the pressure lasts, or till the tube C is opened, as the valve B prevents escape of air through A. C passes just through the cork, and D is the jet tube passing to the bottom of the bottle.



IRREGULAR DISTRIBUTION OF SILICON IN PIG IRON.

By John W. Thomas.

In addition to the silicon determinations published in the last number of this journal (p. 148) I have obtained the following results which show still further the irregular distribution of silicon in pig-iron. The samples for analysis were taken from every other bed of the cast.

	1st Cast.	*2d Cast.*	*3d Cast.*	*4th Cast.*	*5th Cast.*	*6th Cast.*
1st bed	2.040	1.367	2.487	2.407	1.694	1.008
3d "	1.746	1.260	2.338	2.567	1.727	1.101
5th "	1.722	1.671	2.324	2.647	1.718	0.885
7th "	1.787	1.718	2.282	2.366	1.680	0.995
9th "	1.769	1.606	2.171	2.842	1.587	1.008
11th "	1.713	1.101		2.721	1.545	1.018
13th "	1.913					

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When the iron contained soft gray spots the silicon was found to be higher in these spots than outside of them, as shown by the following results :

Soft Gray Spot.	*Outside Gray Spot.*
1.055	0.985
1.087	1.018
0.897	0.785
1.979	1.955
2.908	2.240

LABORATORY CRANE IRON CO., CATASAUQUA, PA.

ABSTRACTS.

APPARATUS AND REAGENTS.

An Apparatus for Reducing the Strength of the Current in electrolytic work is described by Alex. Classen, Ber. **21**, 359, and

A New Form of Voltameter is described by the same author, Ibid. 363.

Preservation of Sulphuretted Hydrogen Solutions.—Lindo, Chem. News, **57**, 173, has tested the statement of Lepage, that solution of sulphuretted hydrogen in water to which glycerine has been added keeps better than the solution in pure water alone, and finds it to be incorrect. Addition of glycerine has little or no effect upon the keeping properties. Camphor and thymol added in small quantities prevent oxidation to some extent, but have no influence upon the escape of gas, which is the main reason for the loss of strength.

Stand for Electrolysis.—Chem. Ztg. **12**, 494. The improvement consists in fastening both binding screws to one

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arm of a retort stand. First comes the socket sliding upon the rod of the retort stand; into this a binding screw with two openings is screwed; to the other end of this binding screw an ebonite piece of the same diameter is fastened and to this a second binding screw like the first. The apparatus can be obtained of Dr. Rob. Muencke, Berlin. A similar apparatus is described by Alex. Classen (Ber. **21**, 365) with two arms instead of one.

A New Arrangement for Rapid Filtering.—P. Raikow, Chem. Ztg., **12**, 661. The apparatus consists of a conical porcelain tube *D* with holes arranged as shown in the cut.

Fig. 1.

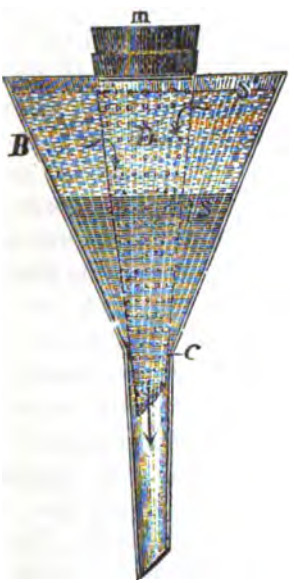
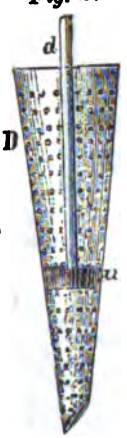


Fig. 2.



Filter paper is wound around the outside of this and the narrow end is pressed into the funnel until it is firm. The solution to be filtered is then poured into the funnel and it passes out as shown by the arrows. When using a filter pump the top of the porcelain tube is closed with a cork *m* or an air tight porcelain stopper, and also the level of the solution *S'* is kept above the upper line of holes. Near the end of the operation when the level of the solution falls below the upper line of holes, the cork *m* is removed and a small tightly fitting rubber cork *u* fastened on the end of the glass rod *d* is pushed down the porcelain tube as shown in Fig. 2. The solution can then only pass through the lower lines of holes The filter papers are cut in strips from 2–4 cm. wide according to the size of the tube, and wound spirally around it beginning at the bottom, taking care to leave none

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of the holes uncovered. The upper end of the paper is fastened with a thread or stuck in between the cork *m* and the tube. S. C.

Apparatus for Filtering Solutions and Washing Precipitates in a Vacuum or in a Specified Atmosphere.—P. Raikow, Chem. Ztg., **12**, 661. The construction of the apparatus as shown in Fig. 1 needs no explanation. After placing the filter in the funnel *B* and closing the latter with the cork *t*, the cocks *o* and *m'* are opened and the solution to be filtered is poured into the flask *A*. The cock *m'* is closed, the cocks *n* and *n'* are opened and the air is exhausted through the tube *b*, after which an indifferent gas is introduced. The cock *m* is then opened and at the same time the cock *o* is closed. The solution passes out of the flask *A* into the funnel *B* but will not rise much above the end of the tube *p* owing to the pressure of the gas in the funnel, so by raising or lowering the tube *p* the level of the liquid in the funnel may be kept at any de-

Fig. 1.

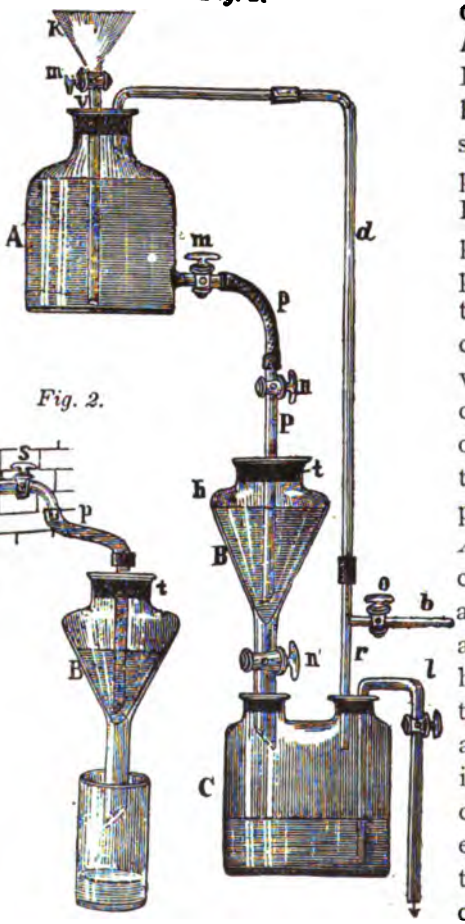

Fig. 2.

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sired height. The filtrate is caught in the bottle *C* and is siphoned off through the tube *l*.

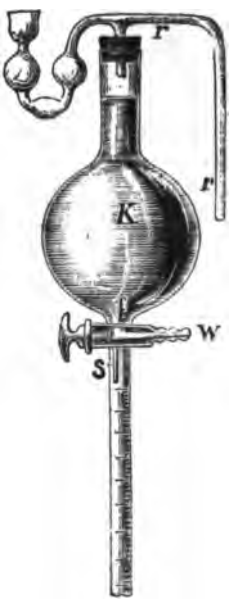
The precipitate is washed in exactly the same manner by placing the washing solution in the flask *A*.

When filtering in a vacuum the cock *o* is closed after withdrawing the air from the apparatus. In this case the solution will fill the funnel *B* owing to the lack of inward pressure.

If the precipitate must be dried in the absence of atmospheric air, the cocks *n* and *n'* are closed, the funnel removed from the tube *p'* and the flask *C* and placed in the drying apparatus where the cock *n'* is opened.

Fig. 2 represents a case where the precipitate can be washed with ordinary water, and the tube *p* is attached to the water pipe. S. C.

A New Measuring Flask for Burettes.—R Schütze, Chem. Ztg., **12**, 722. The flask *K* opens into the burette at *f*. The two-way cock is so arranged that, if necessary, the air may pass in and out of the burette at *S*. If the air must be washed the end of the cock *w* is fastened to the wash tube *r* with a piece of rubber tubing and the bulb filled with the proper solution. The accompanying cut needs no further explanation. S. C.



An Arrangement for Filtering.—R. Hirsch, Ztschr. angew. Chem 1888, **1**, 160. A modification of Witt's apparatus. Witt's filter consists of a funnel in which is laid a round perforated plate covered with asbestus. This plate according to the author is easily displaced, and he therefore uses a special funnel made of porcelain and containing a perforated plate of the same material moulded into it.

Stand for Holding Filters.—A subscriber to Fresenius'

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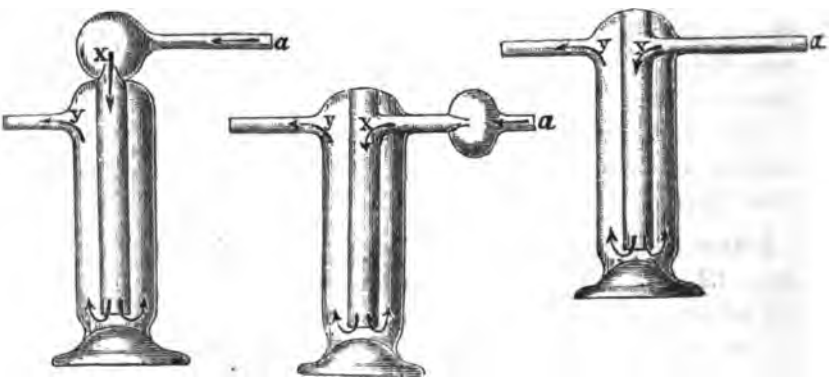
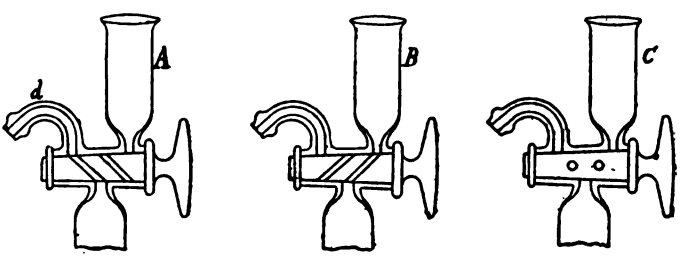
Zeitschrift für analytische Chemie, **27**, 178, states that Meurer's apparatus (this Journal **2**, 78) may be improved by bending the tubes upon which the funnels rest, in and out, so as to form sockets into which the funnels will fit.

A New Form of Drying and Absorbtion Tube.—R. Schütze, Chem. Ztg., **12**, 722. It consists of an inverted bottle with a flat topped stopper which serves for a base.



The tube x is melted in the bottom and the openings at x and y are stopped with a loose wad of cotton or similar material. The flask is filled with the drying or absorbing material through the neck and the stopper is sealed with a thin layer of paraffine. The gas passes through in the direction of the arrows. S. C.

An Improved Form of Nitrometer.—G. Lunge, Ber. **21**,



376. Lunge has improved his nitrometer by using a Greiner and Friederichs stop-cock* instead of the ordinary form.

* See this Journal, Vol. 1, p. 316.

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The accompanying cut shows the stop-cock in three different positions.

A New Siphon for Drawing Off the Upper Part of Liquids.—P. Raikow, Chem. Ztg., **12**, 662. The apparatus is plainly illustrated in Figure 1. To operate, the cock *h* is closed and the cock *h'* is opened. By blowing in the tube *b* of the aspirator arrangement the air in the siphon is rarefied and the solution passes through the hole *o* in the float *n*, and fills the siphon. The cock *h'* is then closed and by opening the cock *h* the solution may be drawn of at pleasure. A pipette, Figure 2, is made on exactly the same principle. S. C.

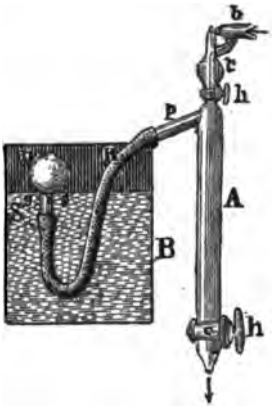

Fig. 2

Purification of Sulphuric Acid.—R. Meldola and E. R. Moritz, J. Soc. Chem. Ind. **7**, 63. The sulphuric acid used for making nitrogen determinations by Kjeldahl's method frequently contains ammonium sulphate. This may be destroyed by adding a small quantity of potassium nitrite (.05 gm. KNO_2 to 10 c. c. acid) and heating for 2¼ to 2½ hours previous to the introduction of the substance to be analyzed. The nitrite destroys the ammonia, and the excess of nitrous acid is driven off by the subsequent heating. A number of test analyses are given to show that all the excess of nitrous acid is in fact driven off.

The Analysis of Explosives.—W. Hempel, Ztschr. anal. Chem. **26**, 312. The author has modified the apparatus for

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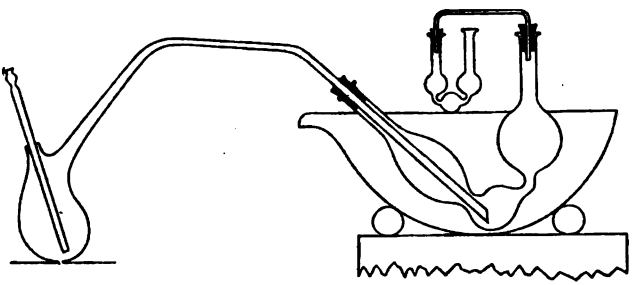
this purpose, already described (Ztschr. anal. Chem. **20**, 82), by the addition of a side tube to the decomposition bulb. This is used to introduce the sulphuric acid. The author prefers his apparatus to that of Lunge, because in Lunge's apparatus the surface of the mercury cannot easily be seen when dynamite is the substance analyzed.

Apparatus for the Estimation of Iodine.—G. Topf (Ztschr. anal. Chem. **26**, 293). The substance is introduced through the small funnel tube which is afterwards connected with a carbon dioxide apparatus, a slow stream being carried through the apparatus during the distillation. The receiver



contains potassium iodide solution, into which the end of the retort neck dips. The form of the apparatus is such that no iodine can come in contact with the rubber cork used to connect the retort with the receiver. If the substance to be treated is insoluble the tube into the retort should be made wider and not reach too near the bottom.

Porcelain Observation Tubes.—Max Müller has used observation tubes made of porcelain in place of the ordinary brass and glass tubes. The thick glass tubes are easily broken on account of unequal cooling of the inner and outer sides. This difference of tension causes the tubes to break readily, especially when the soft inside is scratched in cleaning. Metal tubes are apt to vary in length either by slight bending or changes in temperance. They are also easily attacked by acids. Porcelain tubes combine the advantages of both metal and glass tubes and are free from their defects.

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They are made by Schmidt & Haensch, Berlin. (Zeit. f. angew. Chem. 1888, No. 9, p. 251.)

[NOTE.—I have used glass tubes for many years and have not noticed the tendency to break above mentioned. Porcelain tubes are doubtless just as good as those made of glass, but when required in lengths of 500 cm., would be difficult to get straight and would also be very expensive.—H. W. W]

INORGANIC ANALYSIS.

Separation of Iron, Nickel, Cobalt, Manganese, Zinc and Aluminum.—Thos. Moore, Chem. News **56**, 3; **57**, 125:

"*Nickel from Iron.*—To the cold concentrated (20 to 30 c.c.), and slightly acid solution, add an excess of solid sodium bicarbonate, in such quantity that after stirring a little remains undissolved, and nickel and iron both appear to be thrown down. Now add potassium cyanide until the precipitate dissolves, then heat gently until the pale yellow color of the ferrocyanide is produced; at this stage the solution should be perfectly clear and free from any ferric hydroxide. Allow the liquid to cool; add a considerable quantity of a rather strong solution of potassium hydroxide; then treat with chlorine, continuing the current of the gas until the green nickelous hydroxide is completely converted into the nickelic hydroxide and becomes perfectly black; after which it may be filtered off, and treated in the usual manner for electrolytic deposition."

"*Alumina from Nickel, Iron or Cobalt*—Proceed exactly as above, and add a few drops of potassium hydroxide to the somewhat turbid yellow solution until it becomes perfectly clear; then boil with the addition of ammonium chloride, when the alumina will be precipitated free from any of the other accompanying metals. The potassium hydroxide and cyanide, as well as the sodium bicarbonate for this separation, should be tested for alumina and silica, impurities almost invariably present."

"*Manganese from Iron, Nickel, or Cobalt.*—Add excess of

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sodium bicarbonate and potassium cyanide as already directed, and warm gently until the solution—which in presence of manganese has a dirty blue-green color—becomes pale yellow and quite clear; then allow to cool, add a little potassium hydroxide, and precipitate the manganese as peroxide by adding a little peroxide of hydrogen and leaving the solution in a warm place for a few hours. The peroxide, as is usual when precipitated from alkaline solutions, contains alkali, from which it is very difficult to free it by washing, so that it is best to dissolve in hydrochloric acid and preciptate as carbonate with ammonium carbonate. In order to avoid this inconvenience the cyanide solution may be precipitated by sulphuretted hydrogen, when manganese sulphide is rapidly and completely thrown down, and admits of being easily washed free from impurities."

"*Iron from Zinc.*—Procure a solution of the cyanides as above, and boil the clear solution with an excess of colorless ammonium sulphide until the steam is neutral to test-papers. The zinc is wholly precipitated as sulphide quite free from iron (or nickel and cobalt if present), and in a granular condition, which may be filtered and washed with the utmost ease."

"The presence of cyanates or carbonates in the potassium cyanide exerts no influence whatever on the above separations."

Separation of Tin from Antimony.—H. N. Warren, Chem. News, **57**, 124. Slags containing these metals are treated with hydrofluoric and hydrochloric acids and evaporated to dryness to drive off the silica. The solution is treated with sulphuretted hydrogen and the precipitate treated with sodium hydroxide to separate bismuth and copper. The filtrate is acidified with hydrochloric acid, the precipitate dissolved in aqua regia and the solution evaporated to drive off most of the nitric acid. Moderately weak hydrochloric acid is now added and potassium ferrocyanide added in sufficient excess (the color of the solution should be blue); the solution is brought to a boil and the stannic ferrocyanide filtered off.

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This is dried, ignited with addition of nitric acid, reduced to the metallic condition in a stream of hydrogen or coal gas, dissolved in hydrochloric acid and the tin precipitated as sulphide and determined in the usual way.

The antimony is precipitated from the filtrate with sulphuretted hydrogen and estimated in the usual manner.

Alloys are analyzed in the same manner except that they are dissolved by means of aqua regia. No test analyses are given.

A New Method for the Determination of Stannous Salts.—Adolf Jolles, Chem. Ztg. **12**, 597. Exactly 5 or 10 c. c. of an alkaline potassium permanganate solution are titrated with a solution of the stannous salt which is to be analyzed until the green color changes to a yellowish brown after shaking. The result of this reaction is probably the formation of a soluble double salt which decomposes after a time, according to the concentration of the solution, with the separation of MnO_2. The K_2MnO_4 solution is made by dissolving 4 or 5 gms. K_2MnO_4 and 8 or 10 gms. KOH in a little water and diluting to a liter. The strength is determined by a standard solution of tartar emetic, made by dissolving exactly 10 gms. of the pure salt in water and diluting to a liter. 5 or 10 c. c. of the permanganate solution are diluted to render the reaction more distinct, and the tartar emetic solution is run in from a burette until the green color is changed to a yellowish brown after shaking. The following reaction takes place: $2(C_4H_4O_6KSbO+\frac{1}{2}aq)+2\ KOH+2\ K_2MnO_4=Sb_2O_5+2(C_4H_4O_6K_2)+2K_2MnO_3+H_2O+aq$. The reactions with $SnCl_2$ are these:

$$SnCl_2+2\ KOH+K_2MnO_4=2\ KCl+SnO_2+K_2MnO_3+H_2O.$$
$$K_2MnO_3+H_2O=2\ KOH+MnO_2.$$

This method may be used in the determination of Sb_2O_3 and As_2O_3 by making a solution of either take the place of the stannous solution.*

The reactions are as follows:

$$Sb_2O_3+2\ K_2MnO_4=Sb_2O_5+2\ K_2MnO_3.$$
$$As_2O_3+2\ K_2MnO_4+2\ KOH=2\ K_2AsO_4+2\ MnO_2+H_2O.$$

* Zeits. f. ang. Chem. *1888*, 160 and 261.

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From the above reactions it will be seen that 1 mol. $K_2MnO_4 = \frac{1}{2}$ mol. $Sb_2O_5 = 1$ mol. $SnCl_2 = \frac{1}{2}$ mol. As_2O_3 and from these the calculations are easily made.

In the quantitative determination of commercial $SnCl_2$, such as is used in cloth printing works, there is often $FeCl_2$ present which gives high results. In this case, or if the solution has stood in the air some time and the total amount of tin is to be determined, it is precipitated with metallic zinc and, after being washed thoroughly, it is dissolved with HCl in a stream of CO_2 and the $SnCl_2$ determined as above described. S. C.

Determination of NaCl in the Alkaline Waters from Coal Mines.—L. L. DeKoninck, Chem. Ztg. **12**, 597. Water from coal mines often contains bicarbonate of soda and also some organic matter which colors the liquid and prevents the determination of the chloride by titrating with silver nitrate solution. The author adds 20 c. c. of calcium nitrate solution, free from chlorine, to 200 c. c. of the water to be analyzed and stirs the mixture thoroughly. The precipitate that is formed carries down with it all the coloring matter and leaves a perfectly clear solution which is passed through a dry filter, and 110 c. c. titrated in the usual manner with silver nitrate solution using potassium chromate as an indicator. Instead of calcium nitrate, magnesium nitrate or sulphate, or the corresponding zinc salts may be used. S. C.

The Use of Sodium Pyrophosphate for the Determination and Separation of Metals.—G. Vortmann, Ber. **21**, 1103. Sodium pyrophosphate when added to solutions of the metals produces precipitates which dissolve in an excess of the precipitant with formation of double salts. These double salts are decomposed by acetic acid with the formation of difficultly soluble compounds.

Copper Salts give with sodium pyrophosphate a light blue precipitate which dissolves in an excess of the precipitant with a dark blue color. This remains clear on boiling and gives when boiled with addition of acetic acid a light blue crystalline precipitate, the precipitation is, however, incom-

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plete. If sodium tartrate is added to the blue solution and then acetic acid, the liquid remains perfectly clear on boiling; if it is evaporated to dryness on the water bath the residue will redissolve completely in water; sodium thiosulphate also prevents the precipitation by acetic acid.

Cadmium Salts are precipitated by and redissolved in an excess of sodium pyrophosphate; on addition of acetic acid the cadmium is almost completely precipitated; the separation is complete if the solution is evaporated to dryness and the residue digested with water; sodium tartrate and thiosulphate do not interfere with the precipitation, and copper and cadmium may therefore be separated perfectly by means of this reaction.

Manganous Salts and Zinc Salts behave like cadmium except that the separation of zinc is incomplete in presence of sodium tartrate.

Cobalt Salts give with sodium pyrophosphate a gelatinous precipitate which dissolves in an excess of the precipitant; this solution by shaking or slight warming is converted into a transparent jelly; the formation of the jelly is prevented by the addition of sodium tartrate. When acetic acid is added and the solution boiled the cobalt separates completely as rose red pyrophosphate; presence of sodium tartrate has no influence; if ammonia is added instead of acetic acid, only a part of the cobalt separates.

Nickel Salts behave like cobalt salts; the jelly like mass forms less easily and presence of tartrates prevents the precipitation of the nickel. Ammonia does not produce a precipitate in the solution to which tartrates have been added.

Ferrous Salts give a greenish white precipitate soluble in excess, reprecipitated from a hot solution with acetic acid.

Ferric Salts give a precipitate soluble in excess, not reprecipitated by acetic acid. If to such a solution sodium sulphite and acetic acid is added and the solution boiled, the iron is completely thrown down.

Aluminum Salts give a precipitate, soluble in excess; on addition of acetic acid and boiling the solution all the

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alumina is precipitated; tartrates prevent the precipitation.

Uranous Salts give a precipitate, soluble in excess, not reprecipitated on addition of acetic acid.

Chromic Salts give a precipitate only slightly soluble in excess; addition of acetic acid interferes with the precipitation by sodium pyrophosphate, the solution only becoming turbid; addition of sodium tartrate prevents this turbidity.

From the above statements it is evident that sodium pyrophosphate can be used for separating copper from cadmium, cobalt from nickel, manganese and zinc from iron (ferric), manganese from aluminum and uranium, ferric oxide from aluminum and uranium, possibly also from chromium and iron (ferric).

Cadmium, manganese, zinc, cobalt, nickel, and possibly also iron and aluminum may be determined as pyrophosphates.

Examination of Lead Peroxide.—L. Opificius Chem. Ztg. **12,** 477. Nitric acid of 1.2 sp. gr. is added and then pieces of chemically pure metallic copper. The peroxide dissolves perfectly without the aid of heat. The mixture should be shaken several times to bring the copper in contact with the peroxide. In this way the addition of organic substances to reduce the peroxide is avoided; and this is an advantage, inasmuch as such substances interfere with the precipitation of lead with sulphuric acid: furthermore, it is possible, by using dilute acid, to prevent the solution of any litharge added as an adulterant, and to determine the amount. If copper is present in the peroxide, the amount added must be subtracted from that found.

The Determination of Thallium.— G. Neumann, Ann. Chem. **244,** 349; Ber. **21,** 356. The metal is separated by electrolysis, washed out of contact with air, dissolved in acid and the hydrogen obtained collected and measured; from the volume of hydrogen obtained the weight of the thallium is calculated. The apparatus used is shown in Figs. I, II and III. The flask, Fig. I, has a capacity of 100 c. c.; the platinum electrodes have an area of 9 sq. cm. The thallium salt is

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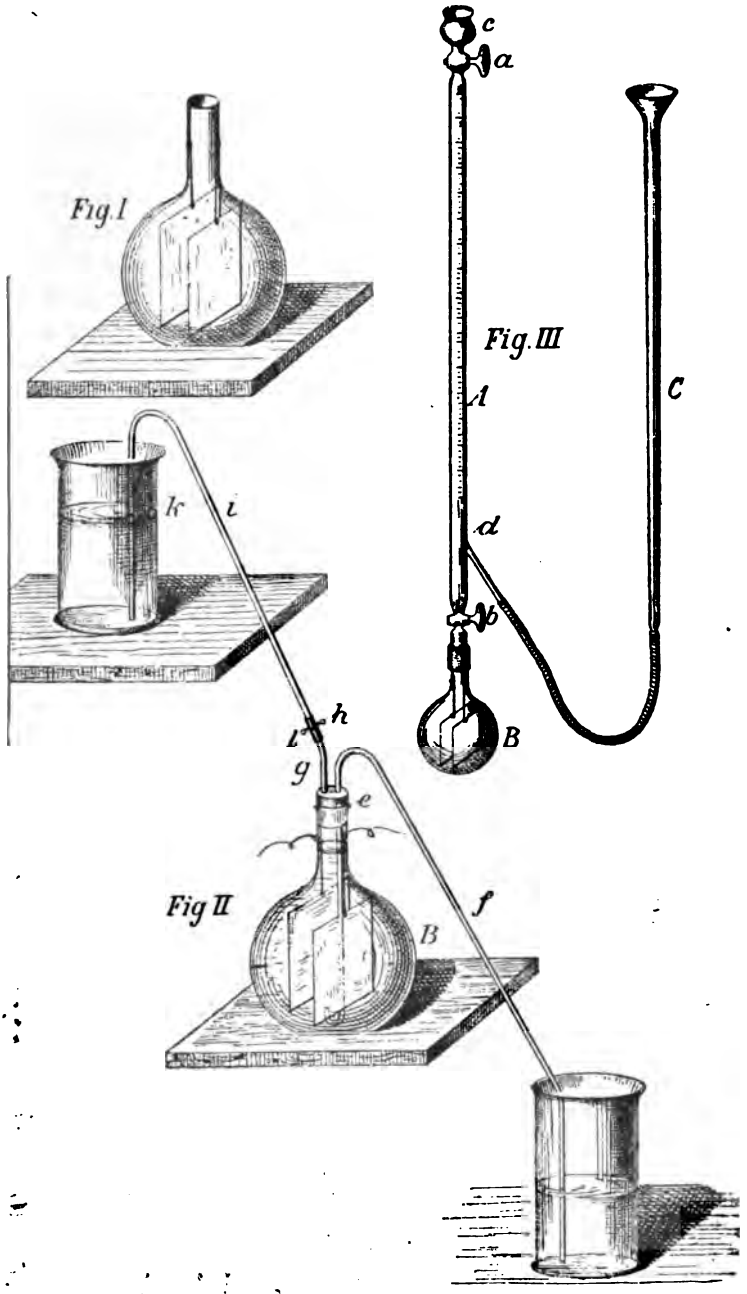

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poured into this flask with about 5 gms. ammonium oxalate, warmed slightly and subjected to the action of a current of 0.1 volt. 0.6 to 0.8 gms. of metal separate in 7 hours and adheres firmly to the cathode. The metal has all precipitated when ammonium sulphide produces no precipitate in the solution. If the metal comes in contact with air it oxidizes, and to avoid this the arrangement shown in Fig. II is used in washing the metal; the figure is self-explanatory. The washing is carried out without interrupting the current; the flask is heated strongly at the end of the operation to drive off gas absorbed by the electrodes. The flask is now connected to the "Hydrometer," Fig. III*, by means of rubber tubing. This hydrometer contains 80 c. c.; the graduation is from the top downwards; the opening in the cock *b* must be at least 0.5 mm. to permit the easy passage of the gas bubbles. The flask is now filled with water until it reaches to the upper edge of the opening in *b*; this is then closed, the apparatus filled with acid and the cock *b* opened; the hydrogen collects in *A* and is measured, reduced to 0° and $760^{mm.}$ and the amount of thallium calculated therefrom. The author obtained 87.31 and 87.02 instead of 87.18 from thallous carbonate; 76.71 instead of 76.69 from thallous nitrate; and 81.13, 81.05, 81.12 and 81.09 instead of 80.98 from thallous sulphate.

Separation and Determination of Boric Acid.—H. N. Morse and W. M. Burton, Am. Chem. J., Vol. 10, No. 2. If borates, silicates and carbonates are in solution and tropaeolin OO and dilute H_2SO_4 are added, no acid reaction is given until all the silicic, carbonic, and boric acids have been liberated. Silicic acid is dehydrated by means of anhydrous copper sulphate. Boric acid, alone, being soluble in absolute alcohol, may be very exactly separated by this means and may be determined as a meta-borate of calcium, magnesium, or barium. The last form is preferred, because the mixture of carbonate and meta-borate of barium is not decidedly hygroscopic, or capable of absorbing CO_2, and hence can be brought more readily to a constant weight, and because the

*See this Journal 1, 419.

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use of barium permits the use of a standard solution of hydroxide. The reagents used are: (1) An aqueous solution of tropaeolin OO. (2) A standard solution of H_2SO_4(1 c. c. = 20 mg. $BaCO_3$). (3) A solution of barium hydroxide approximately equivalent to the H_2SO_4. (4) Dehydrated copper sulphate, prepared by heating the pure salt in an air bath at 150°, until the whole mass assumes a uniform light color. It is not advisable to remove more than four of the five molecules of water of crystallization, else some free H_2SO_4 would be liberated. (5) Absolute alcohol, prepared by digesting alcohol distilled over lime with dehydrated $CuSO_4$ for two or three days.

If the boric acid is in solution, the liquid is made slightly alkaline with caustic potash, then evaporated to a volume of 10 or 12 c. c. If it is in insoluble form, as a silicate, the method is: fuse 4 gms. of solid potassium hydroxide in a nickel crucible to quiet fusion. After cooling, spread the finely ground and weighed material over the fused mass and then heat for two hours at a temperature sufficient to keep the hydroxide melted, and stir frequently with a stout platinum wire. The crucible is then placed in a porcelain dish, and the soluble parts separated by filtering and washing, and the filtrate evaporated to 10 or 12 c. c. as before. If iron is present in the decomposed material, not less than 400 c. c. of water must be used, in order to obtain a complete separation.

To the borate solution is then added a drop or two of tropaeolin solution and dilute H_2SO_4 until an acid reaction is given, the slight excess of H_2SO_4 being carefully neutralized with very dilute caustic potash. The solution which need not exceed 20 c. c., is now thoroughly dried by stirring into it the anhydrous copper sulphate and the mass is then pulverized with a pestle.

The extraction apparatus consists of a narrow Erlenmeyer flask (150 c. c. capacity) and a straight calcium chloride tube, the narrow portion of which is plugged with cotton wool and to its lower end a small glass tube is attached, which reaches to the bottom of the flask when the tube is in position. The

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quantity of dilute $Ba(OH)_2$ solution equivalent to 25 c. c. of the standard H_2SO_4 is run into the flask and the filter pump attached. The extraction tube is then filled with the $CuSO_4$ mixture and absolute alcohol added, till the mixture has become wet, when the pump is shut off, and the mass allowed to soak 15 minutes. Five other portions of the alcohol, 15 c. c. each, are then separately drawn through the tube. The excess of $Ba(OH)_2$ is precipitated by passing into it a current of CO_2, the contents of the flask are poured into a weighed platinum dish, evaporated to dryness and heated till of constant weight.

The proportion for calculation is: Mol. w't of B_2O_3—mol. w't of CO_2 : mol. w't of B_2O_3 : : w't found—theoretical w't of the barium as carbonate : w't of B_2O_3 found.

Results of actual analyses are appended. A. L. W.

The Estimation of Active Oxygen.—For this purpose C. Wurster, Ber. **21**, 921, makes use of paper impregnated with tetramethyparaphenylediamine. One or two drops of the solution are allowed to fall upon a piece of the folded "tetrapaper" which is laid upon an inclined porcelain plate. The paper is then folded again over the drops and, after a few minutes, the color developed in the paper is compared with the color scale. This color scale is prepared by Dr. Schüchardt of Görlitz. The original colors for this scale were prepared by the action of iodine solution upon the "tetrapaper." The scale contains 8 pieces, as follows:

Normal iodine solution corresponding to	$\frac{1}{250}$	$\frac{1}{500}$	$\frac{1}{1000}$	$\frac{1}{2500}$	$\frac{1}{5000}$	$\frac{1}{10000}$	$\frac{1}{33000}$	$\frac{1}{100000}$
shades of color in the scale	I	II	III	IV	V	VI	VII	VIII
and containing milligrams of active oxygen per liter	32	16	8	3.2	1.6	0.8	0.24	0.08

or, if we reckon 16000 drops to a liter

milligrams active oxygen per drop.	0.002	0.001	0.0005	0.0002	0.00001	0.000005	0.0000015	0.0000005

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The tetramethylparaphenylenediamine as it oxidizes becomes first blue and then, on further oxidation, again loses color. In case, therefore, partial bleaching takes place the solution must be diluted with water and a second trial made. The author finds that the juices of many plants color the "tetrapaper" more strongly than $\frac{1}{100}$ iodine solution.

The active oxygen contained in air (nitrous acid ozone, etc.) may be determined by fastening the "tetrapaper" over the end of a glass tube of 0.6 cm. diameter, and drawing the air through it by suction. If the air is too dry the paper is moistened with dilute glycerine.

Estimation of Ammonia by Nessler's Reagent.—Max. Müller describes a colorimeter for the quick and exact estimation of ammonia in water, etc. The colorimeteric apparatus devised by Stammer is used. The tube containing the water to be examined is an ordinary 100 mm. one belonging to a polariscope. The second tube is a metal cylinder arranged to hold one or more discs of yellow glass 1.5 mm. thick, and 24 mm. in diameter. The yellow color of these discs is previously set by a solution of ammonia of known strength, treated with Nessler's solution and observed through a layer 100 mm. in depth.

The discs were six in number and represented the following quantities of ammonia in 100 c. c. water:

1 disc	.02 mg.
2 discs	.05 "
3 "	.07 "
4 "	.10 "
5 "	.15 "
6 "	.20 "

If the water contains more than .20 mg. per 100 c. c. it should be diluted with ammonia free water before the observation is made.

The presence of lime compounds and uncombined CO_2 interferes with the exact determination of ammonia by Nessler's method.

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In all cases, therefore, the water to be examined must be treated with 1 c. c. of a concentrated solution of Na_2CO_3 and NaOH and filtered before the test is applied. Since nearly all filter paper, which has been kept for any length of time contains ammonia the first part of the filtrate must be rejected. By the method indicated the free ammonia in a sample of water may be determined with great accuracy in about five minutes.—(Zeit. f. angew. Chem., 1888, No. 8, p. 245).

H. W. W.

Volumetric Determination of Sulphuric Acid.—A. Gawalowski, Ztschr. anal. Chem. **27**, 152. The solution is carefully neutralized, barium chloride added in slight excess and then sodium carbonate solution until the solution becomes faintly alkaline, phenolphtalein being used as indicator. In presence of ammonia lackmoid is used as indicator, the titration being conducted in monochromatic light (sodium flame).

The substance is dissolved in water, phenolphtalein added, the solution neutralized if necessary, and a slight excess of normal, half normal or decinormal $BaCl_2$ solution added (about ½—1 c. c. of normal solution in excess), the solution allowed to stand half an hour, a few drops of pure alcohol added and titrated with standardized Na_2CO_3 solution until it takes a slight permanent rose color. This point can be hit more sharply by having a solution containing precipitated $BaSO_4$ and $BaCO_3$ for comparison; and by titrating in an Erlenmeyer flask over violet blue paper.

Taken	0.2000	SO_3,	found	0.1992
"	0.4000	"	"	0.4040
"	0.0800	"	"	0.0792
"	0.1200	"	"	0.11992
"	0.1600	"	"	0.16072

The sources of error are: 1st, the slight solubility of $BaCO_3$ in water. 2d, the decomposition of the $BaSO_4$ by the slight excess of Na_2CO_3. 3d, the decrease in solubility caused by the addition of alcohol.

Volumetric Determination of Molybdic Acid and of Lead.—C. Schindler, Ztschr. anal. Chem. **27**, 137. When lead

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acetate is treated with a solution of ammonium molybdate a precipitate of lead molybdate ($PbMoO_4$) is formed, which deposits rapidly when the solution is heated, and is entirely insoluble in dilute acetic acid. The author uses this reaction as a method for the volumetric determination of lead and molybdic acid using tannin as an indicator. This gives with ammonium molybdate solution a blood red to yellow coloration according to the strength of the solution, which is visible in presence of 1 part in 400,000 of molybdic acid. Lead molybdate has no action on tannin solution and lead acetate only in very concentrated solution; even then the coloration produced is different from that caused by molybdic acid. The solutions necessary are:

1. A solution of lead acetate containing 40–50 gms. lead acetate per liter to which some acetic acid has been added. This solution is titrated against ammonium molybdate containing 81.55 per cent. molybdic acid.

2. A solution of ammonium molybdate of such strength that 1 c. c. exactly precipitates 1 c. c. of No. 1, prepared by dissolving the proper amount of ammonium molybdate in water adding ammonia until all turbidity disappears and then diluting to a liter.

3. A solution of .1 gm. tannin in 30 c. c. water. This solution should be used while fresh.

The analysis is conducted by running the lead solution into the solution in which molybdic acid is to be determined until a drop placed upon a porcelain plate with a drop of tannin solution produces no coloration.

The molybdate solution is now added in portions of 1-10 c. c. until the tannin solution produces a faint orange color, and the molybdate solution used subtracted from the lead acetate solution at first run in. The solution in which molydic acid is to be determined should be made slightly acid with acetic acid and should be diluted with hot water to 300–400 c. c.

The estimation of lead is made in the same way, adding the molybdic acid solution to the solution in which lead is to be determined as long as tannin gives the orange coloration.

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Using this method the author found 81.18, 81.36, 81.36 and 81.36 per cent. MoO_3 in ammonium molybdate instead of 81.55, and 0.6703 0.6703 and 0.6713 gms. instead of 0.67045 gms. in a solution of magnesium molybdate.

In lead nitrate the author found 67.46 per cent. lead instead of 67.38 per cent, and in lead white

	By Volumetric Method.	*As $PbSO_4$.*
I	86.33	86.38
II	84.54	84.62
III	86.33	86.46

Since lead forms insoluble compounds with oxalic, sulphuric, chromic and phosphoric acids the method may also be used for the estimation of these acids, an excess of lead solution being added and the excess determined.

The Precipitation of Barium Sulphate in the Presence of Bromine.—Marcel Lucion, Chem. Ztg., **12**, 427. The author finds that the presence of bromine exerts no influence in the precipitation of barium sulphate. S. C.

The Corrosion of Leaden Water Pipes.—Carnelly and Frew. J. Soc. Chem. Ind. **7**, 15.

The Loss of Weight on Igniting Zinc Oxide for a long time in a platinum crucible over the gas lamp is caused, according to Morse and Burton (Am. Chem. J. Vol. x, No. 2), by hydrogen from the flame diffusing through the platinum and reducing the zinc oxide to metallic zinc, which distills off. This reduction does not take place if the oxide is heated in a muffle. Zinc oxide may be heated for many hours in a muffle to a temperature above that required to fuse steel without loss of weight.

IRON AND STEEL.

EDITED BY P. W. SHIMER.

A New Method for the Determination of Manganese.—Leop. Schneider, Monatshefte für Chemie, March, 1888, p. 242. The strong oxidizing power and the distinct red color

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of even the most dilute solutions of permanganic acid have given it an important place in volumetric analysis. In the effort to use these properties for the determination of manganese itself it has been found impossible to completely oxidize the manganese to permanganic acid. Partly satisfactory results have been obtained by oxidizing manganese in nitric acid solution with lead peroxide, and estimating the manganese from the color of the resulting solution. This method, however, only gives useful results with small amounts of manganese. This is due to the high temperature necessary, for lead peroxide oxidizes manganese in presence of nitric acid only at a boiling temperature. Permanganic acid is partly decomposed at this temperature; more rapidly in presence of manganous oxide, with which it forms manganese dioxide which separates as a floculent precipitate which is not further oxidized.

Bismuth tetroxide, on the contrary, oxidizes manganous salts quickly and completely to permanganic acid in presence of large amounts of nitric acid and at the ordinary temperature.

In neutral or slightly acid solutions there is here also the reaction between manganous oxide and permanganic acid resulting in the separation of part of the manganese as peroxide. As the result of many experiments it was found that nitric acid was best for the purposes of this oxidation, and that, in a dilution of 1 milligramme manganese to about 2 c. c. nitric acid, sp. gr. 1.20, at the ordinary temperature, there is, in no stage of the oxidation or reduction, a precipitation of manganese peroxide. When bismuth tetroxide, in finely divided powder, is added to such a solution of manganese in nitric acid, the solution becomes at once dark violet in color. The oxidation of manganese to permanganic acid is complete in a few minutes, especially when the reaction is assisted by frequent shaking of the solution. A mild effervescence of oxygen accompanies the reaction; when this ceases, in presence of excess of the tetroxide, the oxidation is complete. The bismuth tetroxide settles to the bottom and the super-

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natant solution contains all the manganese as permanganic acid. The solution is cleared by filtration through asbestus and the amount of manganese determined by titration.

The following experiments show the rapidity and completeness of the oxidation: 40.5 c. c. of a potassium permanganate solution, such as is used in iron-titration, of which 1 c. c. corresponds to 0.01 grm. iron and which therefore contains 0.0794 grm. manganese, were mixed with 50 c. c. concentrated nitric acid, 60 c. c. water, and the permanganic acid completely reduced to manganous oxide by adding 3 grms. of double sulphate of iron and ammonium. 5 grms. of bismuth tetroxide were added, and, with occasional shaking, allowed to stand at the ordinary temperature. Oxidation began immediately. After ten minutes it was filtered through asbestus, the permanganic acid formed was reduced by addition of an excess of carefully titrated solution of oxalic acid, and the excess of the latter titrated by potassium permanganate solution. This titration gave 0.0792 grm. manganese. On repeating this experiment, 81.0 c. c. of the same permanganate solution was mixed with 50 c. c. concentrated nitric acid and 19 c. c. water, reduced by 6 grms. of the double salt of iron and ammonium and oxidized by 10 grms. bismuth tetroxide. The filtered solution of permanganic acid, after dilution with 150 c. c. nitric acid, sp. gr. 1.20, was titrated as above and gave 0.1583 grms. manganese against 0.1587 grms. manganese present in the permanganate solution used.

These experiments show that manganous oxide is completely oxidized to permanganic acid in strong nitric acid solution by means of bismuth tetroxide, and in presence of considerable amounts of sulphuric acid and oxide of iron.

In the titration of permanganic acid, besides oxalic acid, aqueous solutions of sulphurous acid and hydrogen peroxide were experimented on. Sulphurous acid was found to be unsuitable.

Hydrogen peroxide takes oxygen from permanganic acid and itself completely withstands the oxidizing action of nitric acid. On bringing hydrogen peroxide and permanganic acid

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together, the hydrogen of the former combines with the oxygen of the acid, setting free its own oxygen molecules. ($Mn_2O_7K_2O + 5\,HO_2 = Mn_2O_3 + K_2O + 5\,H_2O + 5\,O_2$.) Reduction is instantaneous; there are no intermediate products and the titration may be accurately carried out with any amount of manganese the solution, as obtained by oxidation with bismuth tetroxide, may contain.

Commercial solutions of hydrogen peroxide contain from 2 to 4 per cent. of the peroxide. For use in volumetric analyses the percentage of peroxide is first determined by means of potassium permanganate and it is then diluted with water so that it contains about 0.5 per cent. 1 c. c. of such a solution corresponds to about 0.003 grms. manganese. In this dilution the solution is permanent enough to be used for several months. When, however, the solution has stood for some time its strength must be determined anew with standard permanganate solution.

For determining the strength of the hydrogen peroxide, so much dilute nitric acid is added to an accurately measured amount of permanganate solution, that 0.001 grm. manganese may be present in 2 c. c. nitric acid, sp. gr. 1.20. The solution to be titrated is allowed to run into the permanganic acid solution (which must be well shaken during this operation) until the final faint red color disappears by the addition of another drop. The dilute nitric acid is prepared by mixing one volume of the strong acid with two volumes of water. Such a mixture has a specific gravity of about 1.20 and remains completely unaltered in diffused daylight. The freedom of the acid from lower oxides of nitrogen is easily tested by addition of a drop of permanganate solution. The resulting red color must not disappear in the course of a few minutes. The presence of free nitric acid in the titration of permanganic acid is desirable, not only because it prevents the precipitation of manganese peroxide during the titration of large amounts of manganese, but it also checks the spontaneous decomposition of very small amounts of manganese, which decomposition takes place more rapidly both in pure water and in solutions of the other acids.

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Commercial hydrogen peroxide frequently contains small amounts of chloride. On the other hand commercial bismuth contains a little silver, which may easily go into the solution to be titrated. On titration, a cloudiness due to silver chloride is produced, which, however, does not hinder accurate titration.

No attempt should be made to separate the silver from the standard solution by means of silver nitrate, for the latter causes a slight decomposition of the standard solution.

In the determination of manganese the method is applied as follows: 5 grms. of steel or pig iron low in manganese is dissolved in 100 c. c. nitric acid, sp. gr. 1.20, and, after the solution is complete, it is boiled for a short time. After cooling about 100 c. c. nitric acid of the same strength is added and the solution digested for some minutes with 10 grms. bismuth tetroxide In the case of irons which contain several per cent. manganese, 1 grm. is dissolved in nitric acid and the solution diluted by addition of 200–300 c. c. of the same acid. Ores or slags which are insoluble in nitric acid, are boiled with hydrochloric acid, and the residue, which in most manganese ores contains manganese silicate, is, after treatment with HCl, transferred together with the acid into a platinum dish and hydrofluoric acid added. Finally a sufficient amount of sulphuric acid is added and the solution evaporated till SO_3 begins to come off.

In the case of high-manganese spiegeleisen, ferromanganese and rich manganese ores, the solution of 1 grm. of substance is diluted with water to one liter, of which 200 c. c. are taken and mixed with 100 c. c. concentrated nitric acid and treated as above with bismuth tetroxide. After complete oxidation of the manganese the solution of permanganic acid is filtered from excess of bismuth tetroxide through an asbestus filter which has been purified by ignition and treatment with nitric acid.

The violet colored solution is transferred from the flask to a high beaker placed upon white paper and titrated with a standard hydrogen peroxide solution until the disappearance

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of the red color. The manner of preparing the standard solution has already been described.

The following are some results obtained by the method:

Substance tested.	*Percentage of manganese by the new method.*	*Percentage of Manganese by other well known methods.*	*Analyst.*
Manganese ore	45.4	45.5 gravimetric 45.2 Volhard	Author.
" "	51.9	51.8 "	"
" "	49 85	49.9 "	Author and Dr. H. Peterson.
Ferromanganese	76.4	76.3 "	Author.
White pig iron	2.80	2.63 gravimetric	Author and Dr. H. Peterson.
Spiegeleisen	10.95	11.0 Volhard	Author and Dr. H. Peterson.
Steel	0.45	0.47 gravimetric	Author and Dr. H. Peterson.
"	0.45	0.48 "	Author and F. Lipp.
"	0.33	0.31 "	Author and F. Lipp.

In order to prepare the bismuth tetroxide, equal parts of bismuth oxide (obtained by heating bismuth subnitrate) and potassium chlorate are triturated together and heated in a wrought-iron dish. The mass glows brightly but does not fuse, neither is there any oxidation of the bismuth oxide. After the glowing is over, two parts caustic soda are added; the mixture fuses at once and quietly to a dark brown mass. The fused mass, when cold, is treated with water until there is no longer an alkaline reaction. The light brown sediment is a hydrous combination of bismuthic acid with soda. If this is stirred up with cold 5 per cent. nitric acid, the soda goes into solution and a dark reddish-brown hydrate of bismuth peroxide settles to the bottom with evolution of oxygen. This is washed first with slightly acidified water, finally with pure water, and then dried.

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The cost of bismuth being considerable, it is recovered from its solution by neutralizing excess of free acid with ordinary soda. Bismuth nitrate is precipitated from the slightly acid solution, which may be ignited and used again for the preparation of the tetroxide.

Composition of Strong Cast Iron.—Thomas Turner, J. Soc. Chem. Ind., March, 1888, p. 200. The author gives the following table of analyses of specially strong cast irons :

	Woolwich Experiments, 1858, Average.	*Silicon Experiments, 1885.*	*Rosebank Irons, 1886.*				*Dumbarton Irons.*		*Wassaic Iron. Average.*
Tensile Strength Tons per sq. in.		15.7	18.2	17.1	16.8	16.4	16.68	15.2	18.46
	Pr. Ct.	*Pr. Ct.*	*Pr. Ct.*	*Pr. Ct.*	*Pr. Ct.*	*Pr. Ct*	*Pr. Ct.*	*Pr. Ct.*	*Pr. Ct.*
Graphitic Carb'n	2.59	1.62	.....	.....	.....	.....	2.90	2.60	2.31
Combined "	.....	0.56	0.36	0.58	0.52	0.40	0.32	0.30	0.78
Silicon . . .	1.42	1.96	1.29	1.50	1.13	1.33	1.34	1.63	1.31
Phosphorus . . .	0.39	0.28	0.56	0.47	0.41	0.70	1.09	1.10	0.29
Sulphur	0.06	0.03	0.06	0.07	0.06	0.05	0.14	0.12	0.08
Manganese . . .	0.58	0.60	1.00	1.00	1.33	0.65	1.38	1.29	1.51

Estimation of Chromium in Iron and Steel.—J. O. Arnold and Henry J. Hardy, Chem. News, **57**, 153. In order to avoid the contamination of chromic oxide by phosphoric acid in the determination of chromium in iron and steel, the authors have devised the following method : In the case of steel about 2 grms. of drillings may be taken for analysis. When the material under examination is a chrome pig-iron, or other rich alloy, about 0.5 grm. in fine powder will suffice. The metal is dissolved in 20 c. c. fuming hydrochloric acid, and the solution is gently evaporated to dryness, so that the brittle cake of chlorides is readily detached from the bottom of the beaker. The mass is broken up with a spatula and brushed into a porcelain dish ; it is carefully crushed to a fine powder by means of a glass pestle and removed to a platinum basin.

The chlorides are then intimately mixed with not less than

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five times their weight of a fusion mixture composed of equal parts of dry sodium carbonate and powdered potassium nitrate; a cover is placed on the basin, and the contents are fused, cautiously at first, over a powerful Bunsen flame, for at least fifteen minutes. The basin containing the fusion is stirred and heated in a beaker containing about 100 c. c. boiling water until the insoluble oxide of iron is completely detached. The dish is then removed. The contents of the beaker are heated for half an hour nearly to boiling; any alkaline manganate present will thus be completely decomposed, and the oxide precipitated, the addition of alcohol as a reducing agent being quite unnecessary.

In order to save time, and to do away with the well-known difficulty of washing the finely-divided ferric oxide without causing some of it to pass into the filtrate, the authors have devised the following plan: At the commencement of the analysis exactly 2.4 grms. of metal are weighed out, the extract and residue from the fusion are carefully transferred to a graduated flask (marked in the neck to contain 301 c. c.), diluted to the mark with warm water, and the temperature carefully noted—the homogeneity of the liquid being first ensured. When the oxides have nearly settled, about 250 c. c. are filtered off through a dry, double filter, into a ¼ liter flask marked in the neck. The liquid is again brought to its original temperature, and is then adjusted to the mark by means of a pipette. The 250 c. c. of clear liquid thus obtained contains the chromium present in 2 grms. of steel.

The yellow chromate solution is placed in a covered beaker and acidified with about 20 c. c. hydrochloric acid, and is then boiled. The nitrous acid liberated from the nitrite resulting from the fusion effectually deoxidizes the chromate. At this stage excess of ordinary sodium phosphate solution must be added (say 10 c. c. of a 10 per cent. solution). The phosphate is now precipitated by means of dilute ammonia, added in the smallest possible excess. The liquid is digested nearly at boiling point till bright and colorless. The precipitate is filtered off (it need not be washed), and is then dissolved off the

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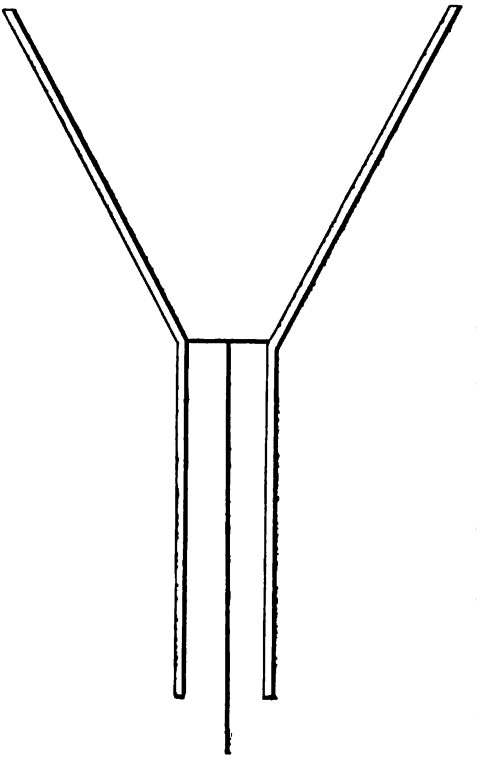
filter with hot hydrochloric acid into the beaker in which the precipitation was made. The bright green solution is boiled down, and finally very cautiously evaporated to dryness. The phosphate is taken up by boiling with a few c. c. hydrochloric acid, and the insoluble residue filtered off. The filtrate, diluted to about 200 c. c., is heated nearly to boiling and treated with diluted ammonia to slight alkalinity. It is digested as before, the phosphate filtered off, gently washed with hot water, dried, ignited, and weighed as $Cr_6P_4O_{19}$ ($3\ Cr_2O_3\ 2P_2O_5$), containing 42.48 per cent. of metal.

A Funnel for Filtering Carbon.—Thomas M. Drown, M. D., Technology Quarterly, May, 1888. The essential feature of the funnel, as shown full size in the accompanying sketch, is the cylindrical stem, the external diameter of which should be a trifle smaller than the internal diameter of the porcelain tube into which the carbon is ultimately transferred for combustion. To support the asbestus which retains the carbon, a flat coil of heavy platinum wire is used, one end of which extends from the center of the coil to a little below the end of the stem. A coil of copper wire may be used in cases where it is not too rapidly dissolved. When the filtration and washing of the carbon



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are completed the coil is removed by pulling on the wire in the stem, and the funnel is set aside to dry.

When ready for combustion, the stem of the funnel is inserted into one end of a porcelain tube, which contains, near its other end, a layer of copper oxide, retained in place by plugs of asbestus. The transferrence of the asbestus and carbon to the tube is very simply and completely effected by means of a glass rod. Any particles of carbon adhering to the glass are easily removed by gentle friction with asbestus.

The advantages of this form of funnel are, first, that the cylindrical stem permits the asbestus to be immediately transferred to the tube without loss; and, second, that the wide upper portion of the funnel allows the liquid containing the carbon to be poured rapidly and freely.

A variation in the usual method of carbon determinations in iron and steel has been successfully tried with this funnel. The iron borings have been placed directly in the asbestus filter, and the solution of the cupric-ammonium chloride has been passed over it by means of a siphon, delivering about a drop a second. From 100 c. c. to 150 c. c. of a nearly saturated solution of the double chloride is sufficient to dissolve all the iron, so that the residue in the filter, which contains some metallic copper, may be washed with dilute hydrochloric acid. It is washed finally with water, dried, transferred to the combustion tube, and burned in oxygen without regard to any metallic copper which may be present.

ORGANIC ANALYSIS.

The Use of Diazo-compounds for the Detection of Organic Substances in Water.—Peter Griess, Ber. **21**, 1830. When Schmitt's parasulphodiazobenzene is added to a water made slightly alkaline which contains organic matter, the water takes a yellow color. The intensity of the color depends upon the amount of organic matter present, and it may therefore be determined colorimetrically in the same way as ammonia. The

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solution of parasulphodiazobenzene must be made up freshly each time as it decomposes slowly with the development of color. The solution is made by dissolving 1 part in 100 parts of water and adding a slight excess of caustic soda. The test may also be applied by adding a little caustic soda to the water under examination, and then a piece of the diazocompound the size of a pin head. 100 c. c. water to which 1–10 c. c. normal human urine has been added and then some some of the diazo solution attains nearly the same color as that produced by Nessler's reagent in the same amount of water to which 1–20 milligram of ammonia has been added. If we remember that phenol, cresol, skatol, indol, etc., are present in animal and vegetable matter there need be no doubt of the cause of this coloration ; gas water, on account of the large amount of these substances present, gives a very intense coloration. Water containing sugar does not give this reaction so strongly. When water to which diabetic urine, containing 6 per cent. grape sugar had been added was tested in this way, much less color was developed than with water to which the same amount of normal urine had been added. Penzoldt and Fischer have used sulphodiazobenzene for the detection of sugar*, but they also add a reducing agent, such as sodium amalgam, and the reaction in this case is quite different.

Determination of Mineral Oil in Animal and Vegetable Fat.—A. Gawalowski, Ztschr. anal. Chem. **26,** 330. A slight error is introduced when this determination is conducted in the ordinary way, caused by the slight solubility of soap in light petroleum in presence of much free alkali. The author avoids this error by adding sodium bicarbonate, bisulphate or alum, after saponifying with alcoholic potassa, and then evaporating to dryness and extracting with light petroleum. The soap is absolutely insoluble in the petroleum under these conditions.

Detection of Saccharin.—E. Börnstein, Ztschr. anal. Chem. **27,** 165. If saccharin is dissolved in 20–30 per cent. caustic potash and bromine added, drop by drop, a yellow pasty pre-

*Ber. **16,** 657.

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cipitate separates. .01 gm. can be detected readily in this way. A better test is founded upon a reaction discovered by Remsen. Remsen found that when orthosulphobenzoic acid is heated with resorcinol a coloring matter analogous to fluoresceine is formed. The author finds that the saccharin behaves like orthosulphobenzoic acid in this respect. The substance to be tested is first acidified and extracted with ether, which dissolves the saccharin (in presence of fat, as in chocolate, the fat is first extracted with light petroleum). The ether is decanted, evaporated to dryness, some resorcinol and sulphuric acid added and the mixture heated until frothing commences, then allowed to cool, slightly heated again and this heating repeated in the same way once or twice. The melt is cooled and dissolved in water; the solution will have a reddish color in transmitted light and a greenish color in reflected light if saccharin is present.

The Detection and Estimation of Magenta in Orchil and Cudbear.—Rawson, Chem. News, **57**, 1483. The author's method is based upon the complete precipitation of the coloring matter of orchil and cudbear in an aqueous and alcoholic solution by basic acetate of lead, followed by an excess of ammonia. From 1 to 2 grms. of cudbear (or an equivalent amount of orchil liquor) are boiled with 50 c. c. of alcohol and afterwards diluted with 100 c. c. of water, 15 to 20 c. c. of a strong solution of basic acetate of lead (sp. gr., 1.25) are then added, followed after stirring, by a similar quantity of strong ammonia. The mixture is filtered, and if the amount of magenta is to be estimated, the precipitate is washed with a solution containing 1 part of ammonia, 5 parts of alcohol, and 10 parts of water; otherwise the washing may be neglected. With pure cudbear the filtrate is colorless; if magenta be present, it is either colorless or pink, according to the amount of ammonia present in the solution. The liquid is then acidulated with acetic acid, when the presence or absence of magenta is at once made apparent; in the case of pure orchil or cudbear, the solution remains colorless, but if a salt of rosaniline be present the well known color of magenta is

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immediately developed. For further proof a piece of worsted yarn may be dyed in the solution, and afterwards tested with hydrochloric acid, caustic soda, and a mixture of hydrochloric acid and stannous chloride.

To determine the *amount* of magenta presents a colorimetric process is made use of. A standard solution of pure magenta, prepared so as to contain 1–100th milligrm. per c. c., is acidulated with acetic acid so that it may be under the same conditions as the solution to be tested. The latter is made up to a known bulk, say 250 c. c. (or if the magenta present be very small, concentrated to 100 c. c., and the whole taken for estimation), and an aliquot part run into a Nessler tube and diluted to 100 c. c. The standard solution of magenta is then run from a burette into a second cylinder in such quantity that the depth of color is equal to that in the first, as in the case of Nesslerizing ammonia. The amount of magenta present can then be readily calculated. In place of Nessler tubes, the colorimeter or Lovibond's tintometer might be used with advantage.

By this method 1 part of magenta has been detected with certainty in 100,000 parts of cudbear. W. W. D.

Loss of Nitrogen by the Soda-Lime Method.—Atwater & Ball (American Chemical Journal, vol. 10, No. 2, p. 113) describe the experiments which they have made to determine the loss of nitrogen in the soda-lime method. The substance selected for a test was casein. Two methods of preparing the combustion tube were followed. In the first, the tube being packed full of soda-lime so as to leave no channel as in the ordinary method; the second, the tube being filled four-fifths to two-thirds, thus leaving quite a large channel. It was proved by this method that when a channel of any considerable size was left the loss of nitrogen was very great. In two instances when the channel was of some considerable size the loss of nitrogen amounted to 68.5 per cent. and 77 per cent. respectively. Trials were also made with strychnine, which resulted in showing that the methods with soda-lime were

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entirely unreliable. The authors summarize the results of their experiments as follows:

1. In combustions with soda-lime, an open space (channel) in the tube is unnecessary and involves danger of loss of nitrogen. This loss may be due to nitrogenous distillation products which escape ammonification, or to dissociation of ammonia, or both.

2. Prolonging the time of combustion unduly may induce loss. The most probable cause of this loss would seem to be dissociation of ammonia.

3. High heat increases danger of loss, probably by dissociation of ammonia, especially when open space in the tube or slowness of combustion, or both, leave the gases for a considerable time exposed to the action of the heat, and not in intimate contact with the soda-lime.

4. With casein (and the data cited and to be cited in the other articles of this series imply that the same is true for the protein compounds of animal and vegetable tissues generally) sufficient contact between soda-lime and substance at moderately high heat suffices to convert all the nitrogen into ammonia. This is effected by intimate mixture of soda-lime and substance, providing a moderately long anterior layer of soda-lime, close packing of the tube, heating the anterior layer well before the heat is applied to the mixture, and keeping it well heated until the operation is done.

5. There are, however, substances, such as strychnine, which, when heated with soda-lime, yield distillation products that are very difficult of ammonification. H. W. W.

The Estimation of Tannin. — Ch. Collin and L. Benoist, Mon. Scien., March 1888, p. 364. This method, like those of Dory, Foehling and Schulze, is based upon the precipitation of gelatine by tannin. To avoid the errors in the results obtained by these methods, caused by the presence of organic acids and various salts, the tannin is estimated volumetrically by means of a standard solution of gelatine, using a derivative of aniline as an indicator. The affinity which some aniline

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derivatives possess for bodies of animal origin is well known. Hence, if a solution of tannin be added to a solution of gelatine, colored by one of these anilines, the coloring matter will be absorbed by the tannate of gelatine as it is formed, and the liquid will become colorless at the point when sufficient tannin solution has been added to just precipitate all the gelatine. Upon these principles the authors have founded the following method :

Standard solutions of tannin and gelatine are very carefully prepared, as also solutions of acetate of lime, methylene blue and Nicholson blue. The tannin, gelatine and acetate of lime solutions are kept free from danger of fermentation by means of the addition of a small quantity of mercuric iodide, dissolved in its own weight of potassium iodide. The methylene blue is used for colored liquids. A measured quantity of the gelatine solution is taken, a few drops of the aniline and some of the acetate of lime solution added, and the whole diluted with warm water. The standard tannin solution is then run into the gelatine by means of an accurate burette, graduated to 1–100 c. c. The liquid is shaken after each additon of tannin. At the instant when the solution becomes colorless the reading is taken. We have thus determined the volume of tannin solution, of known strength, equivalent to the amount of gelatine solution taken. By substituting for the standard tannin solution any other liquid containing tannin and titrating with the gelatine, we can easily determine its percentage of tannin, as the ratio between the volumes of the two solutions required to precipitate the same amount of gelatine will be the ratio between the amounts of tannin contained.

Experiments made by the authors have shown that the method gives very accurate results under the different conditions of various degrees of concentration and the presence of butyrates, gallates, lactates, gallic acid and the salts which accompany commercial tannin. For details and results the reader is referred to the original paper. I. A. P.

The Detection of Cotton Seed Oil in Olive Oil.—Ernest Milliau, Mon. Scien., March 1888, p. 366. This method is

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based upon the fact that the fatty acids of cotton seed oil have a reducing action upon silver nitrate, while the acids contained in olive oil have no such action. 15 c. c. of the oil to be examined is placed in a porcelain dish of 1000 c. c. capacity and heated to 110° C. ; then, while continuing to heat, a mixture of 15 c. c. caustic soda solution, at 40° Beaumé, and 15 c. c. of alcohol, at 92°, is added. As soon as the mixture in ebullition is homogeneous, a sign that saponification is complete, 500 c. c. of distilled water is added, drop by drop, so as not to cool the liquid. After the ebullition has continued a few moments, the fatty acids are separated by means of dilute sulphuric acid (1 part acid to 10 parts water). As soon as the separation is complete and the acid slightly in excess, 5 c. c. of the fatty acids is collected by means of a silver spoon and placed in a small test tube. 20 c. c. of alcohol is then poured over it and the tube placed in the heat of a water bath. When the acids are dissolved 2 c. c. of a solution of nitrate of silver (30 grams silver nitrate to 100 c. c. water) is added and the liquid evaporated to two-thirds its original volume. If the oil taken was pure, the fatty acids remain unaltered ; if, however, it contained any cotton seed oil, part of the silver is reduced and blackens the acids. The test is sufficiently delicate to detect the presence of one per cent. of cotton seed oil in olive oil. The method is all the more valuable because the fatty acids only are tested and thus other impurities cannot influence the results. I. A. P.

Detection of Raffinose in Raw Beet Sugar.—Lotman, Chem. Ztg. **12**, 391, 696, examines raw beet sugar for raffinose in the following way : Take 25 g finely pulverized raw sugar ; shake for an hour with 100 c. c. absolute methyl alcohol, filter and polarize. The raffinose is then precipitated with strong lead acetate (10 c. c. to 100 c. c. sugar solution). The reading of the instrument increased by one-tenth subtracted from the first reading gives the rotation due to raffinose, and thi smultiplied by.162 x 4 shows the quantity of raffinose in 25 g. of the original substance. Example :

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First reading of polariscope	11°
Second " " " 10	6.4°
Difference	4.6°

Then 4.6 x .162 x 4 = 2.98. Therefore 25 g. raw sugar contained 2.98 g. raffinose.

The writer modifies an earlier statement to the effect that raffinose, dextrose, etc., are completely precipitated by lead subacetate both from aqueous and alcoholic solutions so that it reads "only from alcoholic solutions."

NOTE.—The above proceeding is applicable only when the sugar in question contains no other optically active substance than raffinose which is precipitated by lead subacetate. Since raw beet sugar may also contain dextrogyratory pectic products, precipitable by lead acetate, the results may not be altogether reliable. H. W. W.

MINERAL ANALYSIS.

EDITED BY JOHN EYERMAN.

Garnierite from Oregon.—F. W. Clarke (Am. J. Sci., June, 1888) describes and gives analyses of nickel ores from Riddle, Oregon Co., where the deposits are worked by the Oregon Nickel Company.

	Clarke.	*Hood.**	*Hood.**
Loss at 110°C	8.87	6.63	7.00
Loss on ignition	6.99		
$Al_2O_3+Fe_2O_3$	1.18	1.38	1.33
SiO_2	44.73	48.21	40.55
MgO	10.56	19.90	21.70
NiO	27.57	23.88	29.66
	99.90	100.00	100.24

Diamonds in Meteorites.—(Proc. Acad. Natl. Sci. Part I, 1888.) Professor Carvill Lewis exhibited (February 28, 1888) a small fragment of a meteorite which had fallen in the district of Krasnoslobodsk, Govt. of Penza, Siberia, on Sept. 4, 1886, and which he had obtained through the kindness of Mr. George

* Mineral Resources of the United States for 1883.

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F. Kunz. The specimen was of especial interest on account of a report (*Nature*, Dec. 1, 1887, xxxvii, p. 110) that Prof. Latchinoff and Jerofief had detected in the insoluble residue small corpuscles having all the characters of diamonds. The speaker had extracted from the fragment in his possession two small oval bodies with extremely high index of refraction and showing only slight traces of polarization, such as is common to many diamonds. They were colorless and transparent, resembling certain specimens of Brazilian "bort." Having been able to distinctly scratch a polished sapphire with portions of the meteorite, he was disposed to agree with Prof. Latchinoff and Jerofief that these bodies were true diamonds. The olivine in this meteorite was also in the form of oval grains and had a deep yellow color and bright polarization. The rounded form of the olivine and the diamonds may have been due to corrosion of the igneous mass. This rounded form is very commonly shown by the olivines in basic eruptive rocks. While diamonds have never before been found in meteorites, carbon has long been known in them in its graphitic or amorphous form. Recently, Fletcher* has described under the name of Cliftonite a cubical form of carbon, somewhat harder than ordinary graphite, which he found in an Australian meteorite. The important bearing of the present discovery upon the vexed question of the diamond is evident. The speaker had recently endeavored to show that the commonly received notion that itacolumite was the original matrix of the diamond is a mistake, and that diamonds really occur in, or in the neighborhood of basic eruptive rocks.† The facts regarding the associations of the diamond in Africa, Borneo, New South Wales, California and elsewhere, all point to peridotites or allied rocks as the matrix of the diamond. The similarity, both in structure and composition, of the diamond-bearing Kimberlite of South Africa to meteorites had been pointed out by the speaker previously, and he had, in view of this fact, suggested the search for diamonds in meteorites.

* This Journal Vol. I, p. 425. Jour. Minl. Soc. vii, p. 122, 1887.

† Proc. Brit. Assn. Adv. Sci. Manchester, 1887. Geological Magazine, March, 1888.

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Pyrrhoarsenite from Sweden.—Igelström (Bull. Soc. Franc., de Min., IX., 1887, p. 218) gives a description and an analysis of an antimony-manganese *berzellite* from Sjögrufan, Grythyttan parish, Örebro, Sweden.

An old analysis (B) of the Longbaw berzellite is added for comparison.

	A	*B*
As_2O_5 . . . } . . . . Sb_2O_5 . . . }	58.06	58.51
MnO	17.96	2.13
CaO	18.68	23.22
MgO	3.58	15.68
SiO_2	1.02	
H_2O	.85	
$Al_2O_3+Fe_2O_3$	Tr.	
Ign.		0.30
	100.15	99.84

Hardness 4.

Formula $(Ca, Mn, Mg)_3(As\ Sb)_2O_8$.

Bertrandite from Colorado.—S. L. Penfield (Amer. J. Sci. July, 1888, p. 52.) describes Bertrandite from Mt. Antero, Col.

An analysis resulted as follows:

SiO_2	*BeO*	*CaO*	*H_2O*	
51.8	39.6	1.0	8.4	100.8

Gahnite from Rowe, Mass.—Crosby and Brown (Technology Quarterly, Vol. I, pt. 4, 408.) describe and give an analysis of gahnite from the pyrite vein at Rowe Mass. H. 7.5, sp. gr. 4.54.

Al_2O_3 . . } . . . . . Fe_2O_3 . . }	58.05
ZnO	35.91
Ins. res.	1.49
	95.45

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AGRICULTURAL CHEMISTRY.

Estimation of Sugar in Sugar Beets.—Peterman, Pellet, Chevron, Battut and Burkhard have lately made voluminous contributions on the methods of estimating sugar in the sugar beet.

Peterman's full work is found in the Bul. d l'Acad. Royale de Belgique, No. 6, 1887, pp. 2–48. The preference is given to the extraction of sugar from the pulp by alcohol in a Scheibler or some similar apparatus.

As a result of his investigations Peterman reaches the following conclusions:

1. The specific rotatory power of sucrose is the same in aqueous or alcoholic solution.

2. In a beet pulp of sufficient fineness all the sugar can be extracted with 85 per cent. alcohol.

3. Sugar is not decomposed at the temperature of the boiling point of 60 per cent. alcohol.

4. The pulp of a beet properly prepared affords a homogeneous mass, of which 20–25 g. represent an average composition.

5. The process depending on mixing with the beet juice an equal volume of absolute alcohol gives numbers practically equivalent to those obtained by the usual process. Since the cold alcohol does not precipitate the optically active non-sugars this process has no advantage over the old one.

6. The polarization obtained by the alcoholic digestion or extraction of the beet pulp is about .5 per cent. lower than that of the expressed beet juice. This difference depends on the following conditions: (1) The expressed juice does not represent the normal juice of the beet. (2) It contains polarizing non-sugars. (3) The conventional corrective factor .95 is not exactly correct.

7. The digestion of the beet pulp with water removes two of these sources of error, but not the one which depends on the presence of polarizing non-sugars.

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The results of this method are in general, .3 per cent. lower than those of the direct polarization of the juice.

8. The alcoholic digestion gives results which are a trifle higher than those obtained by extraction with the same reagent.

9. The extraction with alcohol of 25 to 50 g. of beet pulp is according to our present knowledge to be preferred to all other methods.

Pellet has described the methods in use by him in La Sucrerie Belge, vol. 16, Nos. 5, 6 and 7.

For beet pulp take 52.1 g. for the 26.048 normal instruments or 32.4 for the 16.20 normal and place in a flask of 200–210 c. c. content marked on neck and divided ½ c. c. Add 175 c. c. water and 5 c. c. sugar of lead solution and fill to 200 c. c. with water. Close with stopper and long glass tube and digest for half an hour at 85–90°. After cooling make up to 201.5 c. c. (to allow for fiber), shake well, filter and polarize. For cane pulp weigh only the normal quantity, and since the cane has twice as much fiber, make up to same volume.

(NOTE.—The method of Pellet was described in full by me in Bul. de l'Assoc. des Chemistes de Sucrerie at de Distillerie 15th Nov., 1884. In the original method the flasks were graduated to 300–310 c. c. with divisions at each .5 c. c. Three times the normal quantity of pulp was used, viz.: 16 19 x 3=48.57 g. A little alkali was added to prevent inversion and the flask closed with air-tight stopper and heated to 100° for one to two hours

Mr. G. L Spencer found that better results were obtained by using only the normal weight of cane chips and polarizing in a 400 to 600 mm. tube. The method as employed now by us is as follows: The cane pulp, chips, or bagasses, having been weighed, are transferred to the flask which is then filled nearly to the mark with water. Some lead acetate is added and also half a gramme of pure precipitated $CaCO_3$. Water is now added so that the volume occupied by fiber is allowed for, and the flask closed. It is now placed in a water bath deep enough to receive the whole bottle and the water raised to the boiling point.

Every 10′ to 15′ the flask is removed and being held by a towel, is well shaken. After cooling the volume is restored to the mark, and the contents emptied into a large mortar. The pulp is well triturated by the pestle and the filtered liquid polarized. The flasks are made by Eimer & Amend and resemble those used for holding liquids charged with CO_2, at high pressure. H. W. W.)

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Battut in Neue Zeit. f. Rübenzucker Industrie, vol. 18, No. 17, p. 181, also recommends the alcohol extraction in place of the old method of juice polarization. An apparatus for the extraction is also described. The author shows in eleven series of analyses the advantages which his process has over alcohol digestion.

Battut gives also in La Sucrerie Belge, vol. 16, No. 19, p. 429, the results of some comparative determinations to establish the differences between the direct alcoholic and aqueous methods.

As a mean of 32 determinations the following numbers were obtained:

By extraction with alcohol according to Battut	13.22	per cent. sugar
By extraction with water	13.48	" "
By digestion with water	13.33	" "

Chevron in an article in La Sucrerie Belge., vol. 16, pp. 1–12, again points out the well known fact that in expressed juices the first flowing is richer in sugar than the juice obtained later at a higher pressure.

Burkhard in a communication published in Neue Zeit. f. Rübenzucker Industrie, vol. 19, pp. 30–34 presents a comparison of the results obtained by the alcohol method in general use in Germany, the extraction method with a Soxhlet-Sickel apparatus and the digestion method as practiced by Rapp-Degener. In the old Scheibler apparatus the alcohol flows constantly through the beet pulp. In the Soxhlet-Sickel method the alcohol after accumulating to a certain volume is drawn off by means of a siphon. In Scheibler's new apparatus the pulp is entirely covered by hot alcohol and this apparatus is recommended as the best for extraction purposes.

The conduct of the digestion-extraction is carried on as follows:

52.1 g. pulp are placed in a flask marked at 201.2 c. c. There are now added 10–15 drops lead acetate solution and filled up to mark with alcohol. The flask is now digested three-fourths

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of an hour at 75°, after cooling made up to mark with alcohol, filtered and polarized.

Weisberg (La Sucrerie Belge, Vol, 16, p. 326), Chevron (Ibid. Vol. 16, p. 365) and Pellet (Ibid. Vol. 16, p. 345) have discussed the influence of pectic bodies on the polarization of beet juices and pulps. The discussion has been allowed to include some matters approaching a personal nature and an abstract would hardly do justice to all the participants. Those interested are therefore referred to the original articles.

Weisberg (La Sucrerie Belge, Vol. 16, pp. 162 and 407), Pellet (Ibid. Vol. 16, pp. 436 and 387) contribute voluminous articles on the influence of lead acetate on polarization.

Weisberg states as the result of his experiments that "the sub-acetate of lead in an alcohol solution of sugar diminishes sensibly its polarization as compared with a corresponding aqueous solution."

"This diminution increases proportionally to the concentration of the solutions."

He further states that the neutral acetate of lead acts in the same manner on the basic salt. The lowering of the polarization is due to the formation of a sucrate of lead insoluble in water and alcohol.

Pellet, as a result of his studies, reaches the following conclusions:

1. That the sub-acetate of lead diminishes the rotatory power of sugar in presence of alcohol, much more than in presence of water.

2. That the difference remains sensibly the same whether the operation is carried on hot or cold.

3. That acetic acid neutralizes almost completely the influence of the subacetate in presence of water or alcohol.

4. That the diminution of the rotatory power is due to the alkalinity of the solution and not the formation of a sucrate of lead.

5. That in any case no insoluble sucrate of lead is formed, since no turbidity of the solution is noticed.

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Detection of Sugar and other Carbo-Hydrates by means of Furfurol.—*Furfurol* is best obtained from bran (whence its name) by treating this substance with H_2SO_4 diluted with three volumes of water and subjecting the mixture to distillation. Its percentage composition is represented by the symbol $C_5H_4O_2$ and its characteristics as an aldehyde by the molecular structure C_4H_3O, COH.

Carbohydrates in general when treated as described above for bran yield furfurol.

Mylius has shown (Zeit. f. Physiol. Chem. Vol. XI, p. 492) that the Pettenkofer reaction for *Gallensäure* (cholic acid) is due to the furfurol arising from the cane sugar employed which with the *Gallensäure* produce the beautiful red-blue colors characteristic of the reaction.

Von Udranszky (Zeit. f. Physiol. Chem. Vol. XII, No. 4, pp. 355 et seq., and No. 5, pp. 377 et seq.) describes methods for detecting traces of carbohydrates by the furfurol reaction which admit of extreme delicacy. The solution of furfurol in water must not contain more than 2.2 per cent. A solution containing 5 per cent. furfurol was found to be most convenient. The furfurol before using should be purified by distillation.

The furfurol reaction proposed by Schiff (Berichte d. deutsch. chem. Gesell Vol. 20, p. 540) appears to be well suited for the detection of carbo-hydrates.

Xylidin is mixed with an equal volume of glacial acetic acid and the solution treated with some alcohol. Strips of filter paper are then dipped in a solution and dried. When these strips of prepared paper are brought in contact with the most minute portions of furfurol, furfuroxylidin is formed [C_4H_3O. CH. $(C_8H_8NH_2)_2$] producing a beautiful red color. A small portion of the substance supposed to contain a carbohydrate is placed in a test tube and heated with a slight excess of concentrated sulphuric acid. The prepared paper is placed over the mouth of the test tube so as to be brought into contact with the escaping vapors of furfurol.

The furfurol reaction with alpha naphthol for some purposes,

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especially the detection of sugar in urine, is more delicate than the one just described. This reaction was first described by Molisch (Sitzungsberichte der Mathematisch-natur-wissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften in Wien, vol. 93, part 2, p. 912) who however, did not understand its real nature.*

The process is carried on as follows: The dilute solution should contain not to exceed .05 to 1 per cent. of carbohydrate. If stronger it should be diluted. Take one drop of the liquid in a test tube with two drops of 15 per cent. alcoholic solution of alpha naphthol; add carefully .5 c. c. concentrated H_2SO_4 allowing it to flow under the mixture. The appearance of a violet ring over a greenish fringe indicates the presence of a carbohydrate. If the substance under examination contain more than a trace of nitrogenous matters, these must be removed before the tests above described are applied.

Analysis by Circular Polarization.—Landolt, (Zeit. d. Vereins f. d. Rübenzucker—Ind., Jan. 1888, pp. 29 *et seq.*; Ber. **21**, 191), has arranged the formulae for determining the percentages of optically active compounds systematically, with a view of giving as safe a base as possible to the calculation of results therefrom.

In the formulae a represents the angular displacement of the polarized ray—(the D or yellow ray) produced by a solution of the body in question at 20°.

$[a]$=specific rotary power.

l=length in decimetres of the tube used.

d=the specific gravity of the solution at 20°.

p=the per cent. of the substance in 100 parts by weight of the solution.

q=the per cent. of optically inactive substances in the solution.

$c=pd$=the concentration, i. e. the number of grammes of optically active substances in 100 c. c. of the solution.

The specific rotatory power $[a]$ is then calculated by the following formula:

* See this Journal 1, 54.

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$$[a]=\frac{100}{l\,c} = \frac{100}{l\,pd}$$

Since the $[a]$ of a substance changes with the concentration of the solution this must be taken into consideration. When the change due to concentration is not a very great one some mean value may be given to $[a]$ by which the content of the optically active substance may be quite accurately calculated, when the concentration does not vary greatly from that mean.

We may use for this purpose the formulae—

$$c=\frac{100}{[a]\,l} \text{ and } p=\frac{100\,a}{[a]\,ld}$$

The value of $[a]$ is different for a solution made up in a 100 c. c. flask graduated at 17°.5 (Mohr's flask) and the same solution measured in a flask at 20° but calculated for a true 100 c. c. at 4°. Thus for sucrose.

$[a]=66.67-0.0095$ c., for the true c. c.
and $[a]=66.82-0.0096$ c., for the Mohr's c. c.

The values of $[a]$ for different values of c. for the two measures are shown in the following table :

	$c.=5$	10	15	20	25	30
True c. c.	$[a]=66.62$	66.58	66.53	66.48	66.42	66.38
Mohr's c. c.	$[a]=66.75$	66.73	66.68	66.63	66.63	66.54

If we take the mean value of $[a]=66.5$ for the true measure then $[a]=66.65$ for the Mohr flask.

From the observed angular rotation for these values—

$$c=\frac{1.5038\,a}{l} \text{ for the true c. c. and}$$

$$c=\frac{1.5004\,a}{l} \text{ for the Mohr c. c.}$$

If the rate of change in $[a]$ is taken into consideration a more exact value of c is obtained from the formula,

$c=0.75063\,a+0.0000766\,a^2$ (true measure) where a represents the angular rotation produced by a layer of the solution 2 dm. in thickness.

Milk Sugar. The $[a]$ of milk sugar has been found to be

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constant up to the value $c=41.5$. It is $[a]=52.53$ (true measure) at 20°.

The variations for temperature=.075 for each degree (correction inversely as the temperature).

Maltose. For maltose the following formula is used:

$[a]=140.375-0.01837\,p-0.095\,t$ (true measure). This formula holds good within the following limits:

p varies from 4 to 35.

t varies from 15° to 35°.

On account of the comparitively small value of the changes the following mean values are assigned.

$[a]=138.3$ at 17°.5 and

$[a]=138.1$ at 20°.

Raffinose (*Melitose*). $C_{18}H_{32}O_{16}\,5H_2O$. The $[a]$ varies but little with concentration. For 20° the mean value is $[a]=104.5$.

Dextrose. The general formula for $t=20°$ is $[a]=52.50+0.0188\,p+0.00052\,p^2$ (true measure). Whence for different values of p the following numbers are found.

$p=5$	10	15	20	25	30
$[a]=52.61$	52.74	52.90	53.08	53.29	53.53

For solutions up to 30 g. in 100 c. c. the mean value $[a]=53.00$ can be assigned for $t=20°$.

Levulose. The $[a]$ varies inversely as the temperature. For 20° the general formula is $[a]=-69.53-0.0935\,p$. The values of $[a]$ for different values up to p at 20° are as follows:

$p=5$	10	15	20	25	30
$[a]=-70$	-70.47	-70.93	-71.40	-71.87	-72.34

The above for aqueous solutions.

In absolute alcohol for $p=7.78$ $[a]=-47$ at 20°.

For each degree between 10° and 40° the value of $[a]$ changes inversely by .5.

Invert Sugar.—For values of p above 68 per cent. the following formula is used at 20° $[a]=-19.447-0.06068\,p+0.000221\,p^2$.

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For lower degrees of concentration at 20° use the expression–

$c =$	5	10	15	20	25	30
$[a] =$	−19.84	−20.02	−20.20	−20.38	−20.56	−20.74

$[a]$ decreases as the temperature rises and for each degree between 5° and 35° this variation amounts to 0.32 for a value of $c = 17.21$.

For more exact calculation use the formulae below–

For values of t between 0° and 30°, $[a]^t = [a]20° + 0.3041 (t - 20) + 0.00165 (t + 20)^2$.

For values between 20° and 100°, $[a]^t = [a]20° + 0.3246 (t - 20 - 0.00021 (t - 20)_2$.

Galactose. For values of t between 10° and 20° and p between 5 and 35 use the value $[a]^t = 83.883 + 0.0785\,p - 0.209^t$. In all the above formulae when not otherwise stated, the true c. c. measure is used, and $[a] = [a]_D$

Molecular Weights of Carbohydrates.—The uncertainty in respect of the true molecular weights of the carbohydrates is gradually disappearing by reason of the insight into the composition of these bodies, which recently discovered physical relations, has permitted.

Raoult, as long as six years ago (C. R. 94, p. 1517) proposed a method of determining molecular weights which is particularly applicable to carbohydrates soluble in water. Further notices of this method by its author are to be found in C. R. 101, p. 1056; 102, p. 1307; and in Annales de Chim. et de Phys. series 5, vol. 20, p. 217, vol. 28, p. 133; and series 6, vol. 2, pp. 66, 93, 99, 115; vol. 4, p. 401, and vol. 8, pp. 289, 317.

The principle of Raoult's discovery may be stated as follows: "The depression of the freezing point of a liquid caused by the presence of a dissolved liquid or solid is proportionate to the absolute amount of substance dissolved and inversely proportionate to its molecular weight."

The following formulæ may be used in computing results:

C = observed depression of freezing point.

P = weight of anhydrous substance in 100 grams.

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$\frac{C}{P} = A =$ depression produced by 1 g. sbstance in 100 g.

T = depression produced by dissolving in 100 c. c. a number of grammes of the substauce corresponding to its molecular weight.

M = molecular weight.

Then we have $T = \frac{C}{P} \times M$.

T is a quantity varying with the nature of the solvent but with the same solvent remaining sensibly constant for numerous groups of compounds.

The value of A $(\frac{C}{P})$ can be determined by experiment. The molecular weight can therefore be calculated from the formula,

$$M = \frac{T}{A}.$$

With organic compounds in water the value of T is almost constantly 19.

Brown and Morris (Jour. Chem. Soc. June 1888 p. 610) report results of their work in extending Raoult's investigations of the molecular weights of the carbohydrates. The process is carried on as follows:

A solution of the carbohydrate is prepared containing a known weight of the substance in 100 c. c. of water. About 120 c. c. of the solution are introduced into a thin beaker of about 400 c. c. capacity. This beaker is closed with a stopper with three holes. Through one of these holes a glass rod for stirring the solution is inserted. The second perforation carries a delicate thermometer graduated to 0°.05. The temperature is read with a telescope. The beaker is placed in a mixture of ice and brine at a temperature 2° to 3° below the freezing point of the solution. The solution is cooled until its temperature is 0° .5 to 1° below the point of congelation. Through the third aperture in the stopper a small lump of ice, taken from a frozen portion of the same solution, is dropped, causing at once the freezing process to begin. The liquid is briskly

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stirred and as the congelation goes on the temperature rises and finally becomes constant. The reading is then taken. The depression in freezing point, controlled by the strength of the solution, should never be more than 1° to 2°.

The method applied to some of the more important carbohydrates gave the following results :

Dextrose.

Calculated for $C_6 H_{12} O_6$.

$M = 180$.

Found $M = 180.2$

As is well known dextrose exhibits in fresh solutions the phenomenon of birotation. The authors supposed that this phenomenon might have some relation to the size of the molecule. They therefore determined the molecular volume of freshly dissolved dextrose by the method of Raoult and found $M = 180$. The high rotatory power of recently dissolved dextrose is therefore not due to any variation in the size of its molecule.

Sucrose.

Calculated for $C_{12} H_{22} O_{11}$

$M = 342$

Found $M = 337.5$

Invertose (Dextrose and Levulose.)

Calculated for $C_6 H_{12} O_6$

$M = 180$

Found $M = 174.3$

Maltose.

Calculated for $C_{12} H_{22} O_{11}$

$M = 342$

Found $M = 322$

Lactose.

Calculated for $C_{12} H_{22} O_{11}$

$M = 342$

Found $M = 345$.

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Arabinose.

Calculated for $C_5 H_{10} O_5$

$M = 150$

Found $M = 150.3$

Raffinose.

Calculated for $C_{18} H_{32} O_{16} 5H_2O$

$M = 594$

Found $M = 528$

Molecular Weight of Raffinose.—Dr. Vries has determined the molecular weight of Raffinose by the method of isotonic proportional numbers described by him in C. r. Vol. 97, p. 1083. By this method the relative molecular weights of all substances capable of plasmolysis in vegetable cells may be determined. The comparison in this case was made with sucrose. The beginning of plasmolysis in the violet cells of the leaves of Tradescantia discolor was used as indicator. The mean of five experiments gave the number 595.7 as the molecular weight of Raffinose. This corresponds to the symbol–$C_{18} H_{32}O_{16}$, $5H_2O. = 594$. This is the composition of Raffinose as determined by Loiseau and Scheibler. (C. r. Vol. 106, p. 751.)

Detection of Sucrose in Unripe Potatoes.—Schulze and Seliwanoff have detected sucrose in young potatoes by the following process : A kilo of dried and finely pulverized young potatoes is extracted hot with 90 per cent. alcohol. The extract is heated to boiling and treated gradually with a hot saturated strontium hydrate solution. The precipitate obtained is filtered, washed with alcohol placed in water and the strontium saturated with carbonic acid. The filtered liquid is evaporated and the syrup extracted with alcohol. This alcoholic liquid furnishes after a time crystals. These crystals by their form, deportment with polarized light, and chemical reactions were proved to be sucrose. The presence of sucrose in the growing potato and its absence in the ripe tubers is a matter of considerable physiological importance. (Biederman's Central-Blatt, vol. 17, No. 3, p. 183.)

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Improvements in Volumetric Methods of Estimating Phosphoric Acid.—Schindler has described improvements in the methods of estimating P_2O_5 by molybdic acid volumetrically, which leads him to affirm that in accuracy it does not yield even to the gravimetric method.

For conducting the analyses the following reagents are necessary.

1. Molybdic acid: To a liter of the molybdic acid solution prepared in the usual way, are added 30 c. c. of a solution, which contains 500 g. citric acid per liter.

2. A concentrated solution of ammonium nitrate, 750 g. NH_4NO_3 per liter.

3. A dilute solution of ammonium nitrate, 100 g. NH_4NO per liter + 10 c. c. HNO_3.

4. Magnesium mixture, prepared as directed in Fresenius' Hand Book.

5. Lead solution of which each c. c. corresponds to about .04 g. P_2O_5; prepared by dissolving 55 g. sugar of lead in one liter of water.

6. Ammonium molybdate solution, of which 1 c. c. corresponds to 1 c. c. of the lead solution. Dissolve about 25 g. ammonium molybdate in one liter of water.

7. Tannin solution: About 0.1 g. tannin in 20-30 c. c. water—to be freshly prepared for use.

The manipulation is conducted as follows:

Take 50 c. c. of the solution of the phosphate in nitric acid corresponding to .5 g. of the substance. Add the concentrated ammonium nitrate solution so that the liquid after precipitation shall contain for each 100 c. c., 25 g. NH_4NO_3. Add the molybdic solution in proportion of 100 c. c. to each .1 g. P_2O_5. Heat in water bath to 58°, allow to stand for 5′–10′ and filter. Wash the precipitate by decantation 3–4 times with 50 c. c. of the dilute ammonium nitrate solution and dissolve it in 3 per cent. ammonia water. Put the solution in a 250 c. c. flask; wash the filter with the dilute ammonia, add 10–20 c. c. of the magnesia mixture, fill up to the mark, shake and filter through a dry filter. Take 50 c. c. of

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the filtrate, acidify with acetic acid and add boiling water to 300–400 c. c. Run out from a burette into the solution lead solution, until there is a slight excess of lead (0.5–1 c. c.), and titrate back with the ammonium molybdate solution. The standardization is fixed by a phosphoric acid solution of known strength. The results are extremely exact. (Ztschr. anal. Chem. vol. 27, No. 2, p. 142).

Estimation of Nitrogen in Soils, Fertilizers, Etc.—Houseau proposes the following mixture for the conversion of all nitrogenous bodies into ammonia in the combustion tube, viz. : sodium acetate, sodium thiosulphate and soda-lime.

The mixture of acetate and thiosulphate is prepared by melting equal parts by weight of the two salts in their water of crystallization and allowing the mass to solidify. After cooling it is reduced to a powder and kept in well stoppered glass vessels. The manipulation is carried on as follows: The combustion tube is closed at one end by fusion. In the closed end are placed first 2 g. of the above mixture and 2 g. of coarsely pulverized soda lime, and then a layer of soda-lime a few cm. in length. Then add the substance containing the nitrogen (.5 g. if rich in N., if soils, etc., 10–25 g.) finely powdered and well mixed with 10 g. of the salt mixture and 10 g. soda-lime. The rest of the tube is filled with soda-lime and last a plug of glass wool or asbestus. The mixture at the bottom of the tube is not heated until the combustion is complete. It is capable of affording about 200 c. c. of gases for the purpose of driving the last traces of ammonia in the receiver. The absorption and titration of the ammonia are conducted in the usual manner. (Abstract in Chem. Central-Blatt, 1888, No. 3, p. 82.)

Estimation of Fat in Milk.—Bruno Röse reviews the methods in common use in Europe for estimating the fat in milk, viz. : the gravimetric methods with gypsum and sand, the procedure with the lactobutyrometer, the areometric method of Soxhlet and the Adams method. The higher results obtained by the latter process he ascribes to a selective absorp-

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tion on the part of the filter paper whereby the milk left in the beaker glass is less rich in fat than the portion absorbed ! His own method is described as follows: About 20 g. milk are weighed in 50 c. c. flask and 2 c. c. NH_4OH added. When the liquid appears clear it is transferred to a separatory burette. This instrument is divided to .5 c. c. and holds about 230 c. c., and is furnished with a glass stop cock and stopper. It is about 60 cm. long and 2.5 cm. in diameter. The graduation is to 200 c. c., leaving room at the top for the necessary shaking of the contents. The small flask is washed with water and alcohol and the washings also poured into the burette. Two washings each of 5 c. c. water, and three each with 15 c. c. alcohol are necessary. For dissolving the fat a mixture of equal parts of ether and light petroleum or benzine is used. A sufficient quantity should be used to bring the total volume of liquid in the burette to 190–200 c. c. The burette is now closed with the glass stopper moistened with water. The burette is now gently shaken for 1′–2′ and set aside for 15′. The volume of the fat solution is next read off. It will be 120–125 c.c. With a pipette 2.5 c. c. of the ethereal solution are removed and placed in a small tared flask. After the most of the solvent has been removed by the water bath, the flask is placed in a glycerine bath at 85–90°, and a stream of dry air drawn through it for 10′. The temperature must not be allowed to exceed 90° to guard against the decomposition which the fat suffers at 100°. The glycerine bath has its great advantage over the water bath in remaining unchanged in volume and from the fact that the glycerine does not attack the glass of the weighing flask as water does, and the flask therefore does not lose weight ! After drying for 10′ the glycerine adhering to the flask is removed by washing with water, and the flask, after cooling, weighed.

(Zeit. für angewandte Chemie, 1888, No. 4, p. 100).

Rōse makes a further communication (op. cit. p. 106) in respect of the loss in weight of fats dried in sand and kept a few days before extraction. In one sample the per cent. of fat fell in three days from 3.22 per cent. to 1.62 per cent. !

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Schreib (Zeit. f. angew. Chem. 1888, No. 5, p. 135) shows that the loss mentioned above must be peculiar to the experiments of Röse. In his own work no such disappearance of fat was noticed.

[NOTE.—Such statements as I have marked ! in the above papers of Röse tend to throw discredit on the whole work, for instance that a small glass flask would lose weight by being kept for 10′ in water at 85°.]

Detection of Nitrates in Waters and Soils.—The qualitative detection of nitrates existing in minute quantities in waters and soils as proposed by Bréal depends on the facility with which they are attracted by capillarity.

Strips of filter paper, free from nitric acid, are dipped into the water or soil to be examined, one end of the strip being supported in the air. As the water rises by capillary attraction and is evaporated the nitrates accumulate on the upper edge of the paper. After 15–20 hours, the upper edge of the paper is cut off and placed in a porcelain dish. After it is dry it is touched with a drop of sulphophenol. If nitric acid be present, a blood-red color is produced, which is changed into blue or green by the addition of ammonia. It is possible to collect all the nitrate contained in a dilute solution on the edge of the paper on the manner mentioned.

In a porcelain dish, with flat bottom, were placed 50 c. c. water and 5 mg. saltpeter. Four strips of filter paper were dipped in the solution. In 36 hours the dish was empty and the strips of paper dry. Sulphophenol placed in the dish gave no color. The strips of paper 1 mm. wide, cut from the upper edges of the filter paper, gave an intense color with the reagent, while a strip of paper cut only 3 mm. from the end gave no color whatever. With soils the results were equally good. By this method it is possible to detect .00025 HNO_3 in a liter of water. (Annales Agronomiques, Vol. 13, p. 322.)

Variation of Fat in Morning and Evening Milk.—The mixed milk from 4 to 16 cows was examined for a year to determine the relative proportion of fat in the morning and evening milk. The morning milking was made at 5 o'clock

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and the afternoon at 4 o'clock. The fat was determined by Soxhlet's areometric method.

The mean percentage of fat in the morning milk for the whole year was 3.33 per cent.
For the evening milk it was 3.82 " "
Mean increase of evening milk, .49 " "

The mean quantity of decinormal alkali required for the distillate from 2.5 g. of the fat treated by Reichert's method was as follows.

Fat from morning milk	14.81 c. c.
Fat from evening milk	14.51 "
Difference	.30 "

It is thus seen that the fat from the morning milk is somewhat richer in volatile acids than that from the evening product.

The author further concludes that the content of easily melting glycerides (butyric, etc.) and the peculiarities of butter dependent thereon, are independent of the food the cow receives, and that the difference between summer and winter butter is to be ascribed to the fact that in the spring and summer the cow is usually in the first stages of lactation. (Nilson, Biederman's Central Blatt, Vol. 17, No. 3, p. 171).

Estimation of Volatile Acids in Butter Fat.—To avoid loss through etherification and failure to evaporate all the alcohol, Mansfield has proposed a method based on saponification without the use of alcohol.

5 g. of filtered butter fat are placed in a flask of the usual shape and dimensions. To the melted fat are added 2 c. c. of a potash solution containing 100 g. KOH in 100 c. c. water. The flask is closed with a stopper carrying a glass tube drawn to a capillary point.

The fat and lye having been thoroughly mixed by rotating the flask, the flask is now heated for two hours in an air bath to 80°–100°, by which time the fat is all saponified. 100 c. c. of water are now added, and after the soap is dissolved it is decomposed with 40 c. c. dilute H_2SO_4 containing 25 c. c.

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concentrated H_2SO_4 in one liter. A few pieces of pumice stone are placed in the flask and 110 c. c. distilled off. The distillate is filtered through a dry filter and 100 c. c. titrated with $\frac{1}{10}$ BaO_2H_2, using phenolphtalein as indicator.

Butters requiring 25.5 c. c. $\frac{1}{10}$ BaO_2H_2 and over are to be considered pure, from 24.5–25.5 c. c. is doubtful, below 24.5 c. c. is adulterated.

(Milch Zeitung 1888, No. 15, and Chemiker Zeitung, Repertorium, 1888, No. 14, p. 120.)

NEW BOOKS.

THE CHEMICAL ANALYSIS OF IRON—By A. A. Blair, 8vo., 282 pages, published by J. B. Lippincott Company, Philadelphia; price $4.00. This valuable work gives full details of the best known methods for the analysis of the raw materials and products of the iron and steel industry. The work contains many illustrations of ingenious mechanical devices for facilitating the work of the chemist; also directions for preparing the reagents used by the iron chemist. Under methods for the analysis of pig iron, bar iron and steel, seven methods for the determination of sulphur are described. Under silicon, four methods are given, one of which is that of S. A. Ford (specially described by Mr. Ford for this volume) by which a silicon determination may be made in twelve minutes from the time the ladle is put into the molten iron. Under phosphorus the acetate and molybdate methods are fully described, although the author is plainly more at home among the details of the former method. F. A. Emmerton describes in detail his rapid method for the determination of phosphorus. Manganese receives its due share of attention, and many interesting pages are given to the determination of carbon. Methods are given for the determination of the rarer elements in iron, but none for the determination of metallic iron in pig iron or steel. Methods in detail are described for the complete analysis of iron ores, limestones, clays, fire-sands, coal and coke, and gases.

The work is a valuable one, recording, as it does, the ripe

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experience of one of the best-known analytical chemists of this country, and it will no doubt facilitate the work of iron chemists, to whom, as the author truly says in his preface, often very little is given and of whom much is required.

P. W. S.

PAMPHLETS RECEIVED.—Chicago, Burlington and Quincy R. R. Boiler Waters. By Walter Lee Brown, Chemist: 214 analyses of waters used by the locomotives of this railroad with explanatory notes.—Wire Rope Tramways. Bleichert System.—The Lunar Society. By H. Carrington Bolton; The Counting-out Rhymes of Children.—Remarks on Early Practice of Vaccination by Dr. Elisha North; Notes on Recent Travel in Europe; Preliminary Notice of a New Study in Folk-Lore; Notes on the Rock-Salt Mines of Petite Anse, Louisiana. By the same author.—The Chemistry of Nitrogen as Disclosed in the Constitution of the Alkaloids; An Address by Albert B. Prescott, Vice Prest. Section C., A. A. A. S.

We have also received the following bulletins and reports: Bulletin of the U. S. Geol. Survey No. 42. Work done in the Division of Chemistry and Physics, mainly during the Fiscal Year 1885–'86.—Missouri Agrl. Exp. Sta. Bull. No. 1.—Nebraska Agrl. Exp. Sta. Vol. 2, No. 3.—University of Texas. Bull. No. 4.—Conn. Agrl. Exp. Sta. Bull. No. 94.—Storrs School Agrl. Exp. Sta. Mansfield, Conn. Bull. No. 1.—Mass. Agrl. Exp. Sta. Bull. No. 29, and Analyses of Commercial Fertilizers, June 1888.—Wisconsin Agrl. Exp. Sta. Bulletins Nos. 12, 13 and 15.—Kentucky Agrl. Exp. Sta. Bulletins Nos. 12 and 13.

NOTES.

—Bailey and Franklin have examined the relative bitterness of different substances; they find it is possible to detect the following amounts when dissolved in water:

Salicin one part in	12,000	parts of	water.
Morphine	14,000	"	"
Quinine	76,000	"	"
Quassin	90,000	"	"

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Picrotoxin	197,000	parts of water.
Aloin	210,000	" "
Strychnine	826,000	" "

The above figures represent an average from 40 individuals. In some of these the delicacy of the sense of taste is much greater than in others. Twelve of these, for example, could detect 1 part strychnine in 1,280,000 water. Some could detect aloin in solutions as dilute as those of strychnine while others could not detect any bitterness in solutions which contained 1 part aloin in 1,250 parts water. The authors find that aloin when kept in solution in water loses its strength. (From a reprint from Transactions Kansas Acad. of Sci., vol. X, sent by the authors).

—We are requested to announce that the twelfth Annual Convention of the Association of Official Agricultural Chemists will be held at the U. S. Dept. of Agriculture, Washington, D. C., on August 9, 10 and 11. All interested in the subjects of the analysis of Fertilizers, Cattle Foods, Dairy Products, Alcoholic Liquors, and Sugar are invited to attend. The Secretary of the Association is Mr. Clifford Richardson, Washington, D. C.

NECROLOGY.—Prof. James C. Booth and Rachel L. Bodley. Short biographical notices will be found in the Journal of the Franklin Institute for July.

A CORRECTION.—The announcement of the death of A. W. Hofmann in the April number was an error. The mistake occurred in the hurry of making up matter for the press at the last moment. Hofmann still lives and reached his seventieth birthday on the date mentioned. We hope he may be spared for many years to enjoy the renown he has so well earned.

ERRATA.

Vol. 1, p. 402, 10th line from bottom, *for* W—2.727, *read* W- 2.7927.

P. 403, 11th line from top, *for* 2.727, *read* 2.7927.

P. 359, 4th line from bottom, *for* 15000 parts free ammonia per million, 2800 albuminoid ammonia, 46000 chlorine, etc., *read* 15.000 parts free ammonia per million, 2.800 albuminoid ammonia, 46.000 chlorine, etc.

P. 429, 2d line from top, *for* Herner, *read* Hehner.

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VOL. II. [OCTOBER, 1888.] PART 4.

THE

Journal of Analytical Chemistry.

A SHORT SCHEME FOR QUALITATIVE ANALYSIS.

BY EDGAR EVERHART, PH. D.

SCHEME FOR THE SEPARATION OF BASES—SUBSTANCES SOLUBLE IN WATER OR ACIDS.

I.—Add HCl drop by drop as long as a pp. forms. Agitate, filter and wash. A pp. may be AgCl, Hg_2Cl_2 $PbCl_2$. (Keep the filtrate for II. It may contain all the other bases.) Proceed with the pp. according to A.

A.—Separation of AgCl, Hg_2Cl_2 and $PbCl_2$: Pour hot water on the pp. in the filter and to the hot aqueous filtrate add H_2SO_4. A white pp. $PbSO_4$.

On the residue insoluble in hot water, pour NH_4OH. If the residue turn black (Hg)″ is present.

Add to the ammoniacal filtrate HNO_3 in excess. White pp. AgCl.

II.—To the filtrate from I, add H_2S in excess, warm, filter and wash. A pp. may be HgS, PbS, Bi_2S_3, CuS, CdS,—As_2S_3, Sb_2S_3, SnS, SnS_2, (Au_2S_3, PtS_2). (Keep this filtrate for III. It may contain all the subsequent bases.)

Treat the precipitated sulphides with yellow $(NH_4)_2S$, warm for a few minutes, filter, and wash. The residue on filter treat according to A, II. It may contain HgS, PbS, Bi_2S_3, CuS, CdS. The filtrate from the $(NH_4)_2S$ solution, treat ac-

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cording to B, II. It may contain $(NH_4)_3AsS_3$, $(NH_4)_3SbS_3$, $(NH_4)_2SnS_2$.

A, II.—The residue containing HgS, PbS, Bi_2S_3, CuS and CdS boil with dilute HCl, and while boiling, if necessary, add $KClO_3$, a very small crystal at a time until the solution becomes clear except for particles of yellow sulphur. Filter off the sulphur and boil the filtrate until the smell of Cl has disappeared. To the solution add NH_4OH in excess, filter and wash.

Pp.—$HgCl(NH_2)$ $Pb(OH)_2$, $Bi(OH)_3$ dissolve in a little HCl and divide into three parts:

a. Add $SnCl_2$: grayish pp. Hg. Or test with copper wire.

b. Add H_2SO_4: white pp. $PpSO_4$.

c. Add a large excess H_2O: white pp. BiOCl.

Filtrate.—Solution of Cu and Cd. Divide into two parts:

a. Acidulate with HCl and add K_4FeCy_6. Reddish brown pp. Cu_2FeCy_6.

b. Add KCN until the blue color of the copper disappears, then add Na_2S in excess: yellow pp. CdS.

B, II.—The filtrate may contain arsenic, antimony and tin as sulpho-salts of ammonium. They may be present as $(NH_4)_3AsS_3$, $(NH_4)_3SbS_3$ and $(NH_4)_2SnS_2$. Precipitate the sulphides by adding HCl in excess. Filter and wash. Reject the filtrate. Dissolve the pp. by boiling with HCl and adding one or two crystals of $KClO_3$. Boil until all smell of chlorine disappears. Filter if necessary.

Put the solution into a side-necked test-tube, together with some zinc and a piece of platinum foil. Conduct the gases evolved into a solution of $AgNO_3$. All of the arsenic and part of the antimony will be volatilized as AsH_3 and SbH_3, respectively.

Volatilized and retained by the $AgNO_3$, As and Sb. Filter the $AgNO_3$ solution and to the filtrate add very cautiously NH_4OH. A yellow ring between the two liquids indicates arsenic. Antimony need not be tested for here. It will be found however in the residue on the filter.

Reduced by the zinc, Sn and Sb. The latter will be indi-

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cated by the dark stain adhering to the platinum foil.

Remove the Zn from the precipitated Sn and dissolve the latter in HCl. Filter from the insoluble Sb, add to filtrate $HgCl_2$, gray pp. Sn.

III.—The filtrate from II. boil to expel H_2S and oxidize by means of a few drops of HNO_3. The treatment of this filtrate will depend upon the absence or presence of phosphates, borates, oxalates, silicates, fluorides, etc., of the alkaline earths, and of magnesia. To decide this point add to a little of the solution to be tested an equal quantity of tartaric (or citric) acid and then ammonia in excess. A pp. indicates the presence of such salts: proceed then according to A, III. No pp. however indicates their absence; in that case proceed according to the scheme in B, III.

A, III.—Divide the filtrate from II into two unequal parts; proceed with the larger part according to B, III.

To the smaller part add an equal bulk of tartaric (or citric) acid, then NH_4Cl, NH_4OH and $(NH_4)_2CO_3$. Warm, filter, and wash the pp. Reject the filtrate. The pp. may contain the precipitated alkaline earths and magnesia. Ignite the pp. on platinum foil. Dissolve the ignited residue in HCl, render alkaline with NH_4OH and then acidify slightly with $C_2H_4O_2$.

Add to slightly acidified solution K_2CrO_4. Pp. $BaCrO_4$. Filter. Divide the filtrate into two unequal parts. To the smaller part add $CaSO_4$ and allow to stand twenty minutes. A pp. $SrSO_4$.

To the larger part of the filtrate add K_2SO_4, warm and filter. To the filtrate add $(NH_4)_2C_2O_4$. A pp. CaC_2O_4. Filter off the pp. and to the filtrate add NH_4OH to alkaline reaction and then Na_2HPO_4. A white pp. $MgNH_4PO_4$.

B, III.—To the filtrate from II which has been freed from H_2S and oxidized, add NH_4Cl, NH_4OH and $(NH_4)_2S$. Warm, filter, and wash. (Keep the filtrate for IV. It may contain all the subsequent bases.) The pp. may contain CoS, NiS, FeS, MnS, ZnS, $Al_2(OH)_6$, $Cr_2(OH)_6$, phosphates of the alka-

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line earths, etc. Treat without heating the pp. with a very dilute solution of HCl. Filter and wash.

The pp. may contain CoS, NiS. Dissolve in aqua-regia, evaporate to dryness. Take up residue with a little water and $C_2H_4O_2$. Add to the solution KNO_2 and allow to stand 12 hours. A yellow pp. indicates Co. Confirm with borax bead. Filter off the pp. of Co and to the filtrate add NaOH in excess. A green pp. $Ni(OH)_2$. Confirm with borax bead.

The filtrate may contain salts of Fe, Al, Cr, Mn, and Zn. Boil the filtrate to expel H_2S, oxidize with a few drops of HNO_3 and add to it Fe_2Cl_6 until a drop of the solution is precipitated yellow by NH_4OH. Concentrate by evaporation to a small bulk, add Na_2CO_3 till nearly alkaline, and finally rub up the solution with an excess of $BaCO_3$. Allow to stand a few minutes and filter. (Fe must be tested for in the original solution by means of K_4FeCy_6 or K_3FeCy_6.)

The pp. may contain Cr and Al. Boil for some time with NaOH and filter.

The pp. contains Cr. Fuse on Pt. foil with Na_2CO_3 and $NaNO_3$. Dissolve in water and to filtrate add $Pb(C_2H_3O_2)_2$. A yellow pp. $PbCrO_4$.

Filtrate contains Al. Acidify with HCl and then add NH_4OH in excess. A pp. $Al_2(OH)_6$.

The filtrate may contain Mn and Zn. Add a few drops of $C_2H_4O_2$ to acid reaction. Then H_2S, filter and wash.

The pp. is ZnS. Dissolve in HCl, boil, add excess of NaOH. Filter if necessary and add $(NH_4)_2S$, Pp. ZnS.

Filtrate contains Mn. Precipitate with NaOH. Filter and fuse pp with Na_2CO_3. A green color indicates Mn.

IV.—The filtrate from B, III, acidify with HCl boil to expel H_2S, filter if necessary, and test for the alkaline earths and magnesia if they have not already been sought for in A, III. To this end add to the clear filtrate NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$. Warm, filter and wash. (Keep the filtrate for V.) The pp. may be $BaCO_3$, $SrCO_3$, $CaCO_3$. Dissolve the pp. by boiling with $C_2H_4O_2$. Cool, and to the solution add K_2CrO_4. A pp. $BaCrO_4$. Filter and divide the filtrate into two unequal parts.

To the smaller part add $CaSO_4$. Warm, allow to stand 20 minutes. A pp. $SrSO_4$. To the larger part of the filtrate add K_2SO_4, warm and filter. To the filtrate add $(NH_4)C_2O_4$. A pp CaC_2O_4.

V. To the filtrate from IV, add Na_2HPO_4 and allow to stand a few minutes. A crystalline pp. $MgNH_4PO_4$.

VI. Test the original solution for ammonia. Test the original substance for sodium by the flame test. If there is reason to suspect the presence of potassium it should be sought for in the filtrate from V, according to Fresenius.

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SCHEME FOR THE SEPARATION OF THE ACIDS.

If As and Sb have been found among the bases, they must be removed before the acids can be tested for. This may be done by precipitating in acid solution with H_2S, filtering (rejecting the pp.), boiling the filtrate to expel H_2S, and proceeding with the acid filtrate according to the next paragraph.

In testing for the acids, it is most important that they should be combined only with the alkalies. This may be effected sufficiently for the purpose by boiling the solution of the substance with Na_2CO_3 in excess. Boil for a few minutes and filter. Reject the pp. The filtrate will contain all the acids combined with sodium.

Add to the filtrate HNO_3 to slight acid reaction, and boil to expel CO_2.

To one-third of the solution containing the acids add $BaCl_2$. Boil for a few minutes and filter.

The pp. $=BaSO_4$.	To the filtrate add NH_4OH just to alkaline reaction and then $C_2H_4O_2$ just to acid reacton, and finally $CaCl_2$.				
	The pp. may be CaC_2O_4, CaF_2. Wash and treat with cold dilute HCl and filter.		The filtrate render alkaline with ammonia and allow to stand a few minutes. A pp. may be $CaHPO_4$, $CaC_4H_4O_6$ or calcium silicate. Filter. Test a portion of the pp. by means of the microcosmic salt bead for SiO_2.		
	Residue CaF_2 Confirm by treating the original substance with H_2SO_4 etc.	Filtrate—CaC_2O_4. Add NH_4OH in excess. A fine pulverulent pp.—CaC_2O_4.	The pp.—$CaC_4H_4O_6$, $CaHPO_4$. Treat with cold NaOH and filter. Residue—$CaHPO_4$ Dissolve in HNO_3 and test with ammonium molybdate.	Filtrate—Boil. A pp. $CaC_4H_4O_6$.	The filtrate may contain organic acids. Proceed according to Fresenius.

To a small portion of the solution, add $AgNO_3$. No pp. indicates the absence of HCl, HBr, HI, HCN, HSCN, H_4FeCy_6, and H_3FeCy_6. If a pp. be obtained :

Test a small portion of the solution with Fe_2Cl_6. A blue pp. H_4FeCy_6 ; a red color HCNS ($C_2H_4O_2$).

Test a small portion of the solution with $FeSO_4$. A blue pp. H_3FeCy_6.

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Test a small portion of the solution with a mixture of Fe_2Cl_6 and $FeSO_4$. A blue pp. HCN.

If the preliminary examination failed to show the presence of I, Br, or CN, then the white pp. first given by $AgNO_3$ can be taken as AgCl. Have these substances been indicated, however, proceed as follows:

Into a side-necked test tube or small retort put a little of the original solution of the substance and then some $Fe_2(SO_4)_3$. Distil, condense the distillate and test it for I with CS_2. After all the I has been expelled from the retort, add some $KMnO_4$ solution; distil, condense the distillate and test it for Br with CS_2. Expel all the Br from the retort and add to the solution remaining in it a little HNO_3 and $AgNO_3$. A white pp. AgCl.

If HNO_3 has not already been found it can be tested for by any suitable method.

Test for H_3BO_3 by the flame coloration or by means of turmeric paper.

CO_2, H_2S, SiO_2, H_2O, etc., should have been found during the preliminary examination.

UNIVERSITY OF TEXAS, AUSTIN, TEXAS.

COMPARISON OF METHODS OF TESTING INDIGO.

BY CHRISTOPHER RAWSON, F. I. C., F. C. S.

A paper by Helen Cooley, S. B., on the "Comparison of Methods of Testing Indigo" has recently appeared in the *Journal of Analytical Chemistry* (II. 129) and in it, one of two processess devised by me some six years ago is criticised. The method to which I refer, and which may be described as the "modified permanganate" or "salting out" process, was first published in the *Journal of the Society of Dyers and Colorists* (I. 75) and subsequently appeared in the *Chemical News* (**51**, 256), which latter journal Miss Cooley quotes. The reference given, however, is p. 255, which is entirely devoted to a

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description of my gravimetric hyposulphite process, which is not even mentioned in her paper. The "modified permanganate," which is described by Miss Cooley as "Rawson's method," is not given quite correctly, and if her instructions were strictly followed they would probably lead to some error. The principle of the process is based upon the precipitation of sulphindigotic acid by a saturated solution of sodium chloride. The precipitate is collected upon a filter, and after washing with a solution of salt is dissolved in water and titrated with $\frac{N}{50}$ solution of potassium permanganate.

Miss Cooley draws the following conclusions—the table is abridged :—"Rawson makes an allowance of 0.0008 grm. indigotin for the amount remaining dissolved in the salt solution. This is sufficient in the case of indigotin, but certain indigoes were found from whose solution salt refused to precipitate the sulphindigotic acid with any completeness. In spite of this fact the method gives generally too high results, and the precipitation of the sodium salt cannot be accomplished without bringing down other organic matter."

	METHODS.			
	Lee.	McKinley.	Fritsche.	Rawson.
Kurpah Blue	56.34	62.00	55.21	——
Guatemala	47.03	62.56	47.10	——
Oude	52.58	52.50	52.72	51.88
Bengal Red	55.99	62.16	53.79	64.10
Bengal Blue	57.54	64.27	57.06	60.89
Indigotin	94.88	——	99.10	——

"It is evident from this table that certain samples of indigo offer much greater analytical difficulties than others. It is not improbable that the claim of merit for certain analytical processes may have come from tests made upon a single sample of indigo. If McKinley's and Rawson's methods were to be judged by the results obtained in the analysis of the Oude indigo, they would be pronounced excellent methods."

Miss Cooley has apparently been working under the impression that Fritsche's method gave perfectly accurate results, and that the value of a sample of indigo was determined by the

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percentage of indigotin which it contained. But further study would no doubt have convinced her that neither of these premises was correct. Fritsche's method is based upon the reduction of indigotin by an alkaline and alcoholic solution of grape sugar. As described by Miss Cooley, this process might give the correct percentage of *indigotin*, but since indirubin is soluble in alcohol this valuable coloring matter would be left in solution on submitting the reduced "liquor" to oxidation. Indigo testing and the estimation of *indigotin* are two very different matters. Some qualities of indigo contain mere traces of indirubin, whilst others contain comparatively very large quantities. A sample of African indigo which I examined a few weeks ago contained 8 parts of indirubin to 32 parts of indigotin. If this sample had been valued upon the percentage of indigotin *only* which it contained, the error would have been equal to at least 20 per cent.

Regarding the difference between Fritsche's method and my "modified permanganate" process, three examples only are given in Miss Cooley's paper. In the case of Oude, the results obtained by the two methods are practically the same, which is no doubt due to that sample containing very little indirubin. The sample marked "Bengal Blue" gives nearly 4 per cent. higher results by my method than by Fritsche's, but since the latter represents indigotin only, the difference may be easily accounted for by that amount (4 per cent.) of indirubin being present. The third sample, viz.:—"Bengal Red" exhibits a difference of 10 per cent. by the two methods. Part, at least, of this difference is again due to indirubin, but unless a very abnormal sample (and such do exist) it is not likely that as much as 10 per cent. would be present. However, there is no proof whatever to show that the difference is due to any error in my process. Miss Cooley states that the method gives generally too high results on account of the precipitation of other organic matter with the sodium sulphindigotate. If such were really the case, one would expect *Oude* and low Kurpah indigoes, which contain relatively far more "organic impurities" than Bengal indigo, to give much higher

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results. But Miss Cooley's own figures point in the opposite direction. It is further stated that "certain indigoes were found from whose solution salt refused to precipitate the sulphindigotic acid with any completeness." This phenomenon was no doubt caused by the mixture of indigo and sulphuric acid having been exposed for too long a period at too high a temperature. I have analyzed about 5,000 samples of indigo of all classes and descriptions, and have never experienced any difficulty of that kind. A great many of these analyses were confirmed by my gravimetric hyposulphite process, and controlled by experimental dye-trials. Furthermore the results, in many cases, have been carefully tested and confirmed on the large scale in more than one dye-house—both by "vat-dyeing" and by indigo-extract dyeing. Whenever the value of indigo is to be determined by processes necessitating the use of sulphuric acid it is most important that this acid should be pure. If the acid contain nitrogen compounds, part of the indigo will be destroyed; and if arsenious acid be present the results obtained will be too high. The "modified permanganate" process when carried out with due care yields results which, for all practical purposes, are trustworthy and reliable. But, as was stated in my original paper on indigo testing,* I consider that my gravimetric hyposulphite method gives the best results of any process which has hitherto been published. Since the method was first published I have introduced a slight modification which may be briefly mentioned here. Although with care the precipitated indigotin and indirubin may be obtained free from "impurities," there are certain cases which present some difficulties. In order to avoid any possible error, therefore, I dissolve an aliquot part of the dry precipitate in sulphuric acid, dilute to a given bulk with water and titrate a portion of the liquid with a standard solution ($\frac{N}{50}$) of potassium permanganate.

3, UNION STREET, BRADFORD, ENGLAND.

* Journal of Society of Dyers and Colorists, vol. 1, p. 75.

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THE ELIMINATION OF ARSENIC IN PHOSPHORUS DETERMINATIONS.

By E. D. Campbell.

Dissolve the ore as usual by digestion in strong HCl or digestion after fusion in cases where the P is insoluble, then add 2 grms. $H_2C_2O_4$, crystallized and evaporate as usual to complete dryness. The As_2O_5 will be reduced to As_2O_3 by the $H_2C_2O_4$ and volatilized as $AsCl_3$ by the strong HCl. When dry, superheat for a few minutes, remove, dissolve in HCl and H_2O and filter off the SiO_2. To the filtrate, add an excess of strong HNO_3 and boil down to 10–15 c. c., or until all the HCl is destroyed. From this point continue as in the regular method for phosphorus by the molybdate method, either weighing the ammonium phospho-molybdate direct or converting to magnesium pyrophosphate. The following results will show that almost a complete elimination of the arsenic may be effected in this manner, and yet that the oxalic acid does not interfere with the ordinary phosphorus determination.

Ore.	As. Added.	P. Regular Method.	P. $H_2C_2O_4$ Method.
Chapin	2.00 per cent.	.061	.070
"	2.05	.071	.082
"	1.13	.064	.066
"	1.12	.062	.066
"	0	.062	.062
Jackson	0	.116	.110
Minnesota	0	.061	.061

The arsenic where it does not exceed 1 per cent. is thus almost entirely eliminated. This method may be applied to pig-iron by dissolving in HNO_3 and adding HCl, evaporating to dryness, then dissolving in strong HCl, adding $H_2C_2O_4$ and evaporating a second time. After the second evaporation proceeding as usual for phosphorus in ores.

Dayton, Tenn., Aug. 4, 1888.

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A NEW METHOD FOR DETERMINING FAT IN MILK*

By F. G. Short.

The possession of a quick, accurate and inexpensive method for determining the total fat in milk, simple enough to be used by persons of ordinary education who have not been trained in the chemical laboratory, is of the highest importance to all persons engaged in handling dairy products. The demand for such a method, if it can be found, is apparent on all sides, for without it a large amount of guess work, if it cannot be characterized by the stronger word ignorance, must continue to impede our progress toward a higher standard in dairy matters. Not only does the demand come from the butter and cheese factories where the need of such a method is keenly felt, but also there are loud calls for it from dairymen and breeders of dairy stock. The practical dairyman desires to keep only such animals as will yield a profit for the feed consumed, having no practical way of testing his cows except by setting the milk from each separately and churning the cream it produces, he finds the method too tedious and requiring so much time that it is given up, and he proceeds along the old path, gauging the ability of the individuals of his herd by the apparent quantity in milk given and the length of time a good yield is maintained.

The breeder of dairy stock is no better off and although he may weigh the milk from each animal and keep careful records, he knows that this tells but part of the story, for it is quite possible that some individual in the herd giving the smallest number of pounds of milk during the year may have due her the largest total yield of butter fat. In order to weed out the herd and breed in butter lines intelligently something like an exact knowledge of the butter production of each individual must be known.

No discussion will be entered upon at this point as to whether or not the fat content is a fair gauge of the quality of milk, for this is largely assumed by all who handle it; and this standard of judgment will without doubt continue in the future. It is not saying too much that if any great advance-

*From 5th Annual Rep. of the Wisconsin Agrl. Exp. Sta.

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ment is to be made in dairy matters in the future, be it with a single cow or the whole herd, in creameries or cheese factories, such advancement will have its foundation upon a quick, accurate and simple method of total fat determination ; if this cannot be found, our progress is greatly delayed if not altogether impeded. At the suggestion of the Director of this Station, the writer some nine months ago undertook to see what could be done for the dairymen in this regard, and has since that date devoted his time largely to the discovery and perfecting of the method herewith described.

THEORY OF THE PROCESS.

The process depends on the following facts : That when a mixture of milk and a strong alkali is heated to the temperature of boiling water for a sufficient time, the fat of the milk unites with the alkali and forms a soap which is dissolved in the hot liquid ; at the same time the casein and albumen are disintegrated and become much more easily soluble. After the heating has continued for about two hours the mixture of milk and alkali becomes homogeneous and of a dark brown color. On the addition of an acid the soap is decomposed, the fatty acids are set free, and rise to the surface, while the albumen, casein, etc., are first precipitated and then dissolved. The insoluble fatty acids, thus obtained, constitute very nearly 87 per cent. of the total fat in the milk.

APPARATUS.

The process requires the following apparatus :

Tubes, Fig. 1, made of soft lead glass about one-sixteenth inch thick. The lower part of the tube being about five inches long and fifteen-sixteenths of an inch in diameter. The upper part of the tube five inches long and one-fourth inch inside diameter.

2d. Three pipettes, Fig. 2, one holding when filled up to the mark B, on the neck, 20 cubic centimeters, (about two-thirds of an ounce), this being the exact amount of milk to be taken for analysis ; the other two pipettes holding ten cubic centimeters each, for measuring the alkali and acid used.

3d. A scale, Fig. 3, divided in millimeters for measuring the column of fat, when the analysis is finished. The one

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Fig. 1

Fig. 2

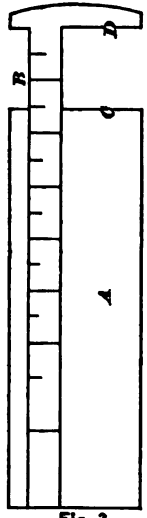

Fig. 3

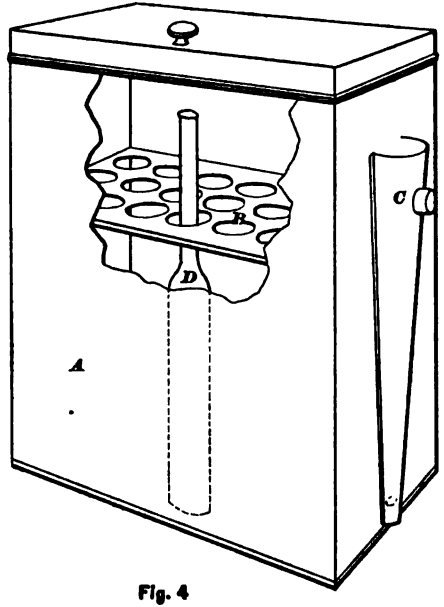

Fig. 4

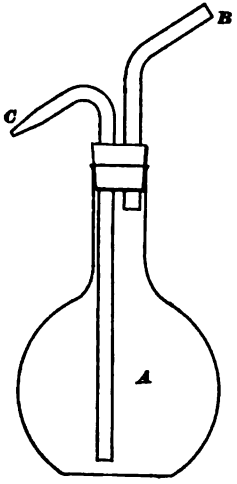

Fig. 5

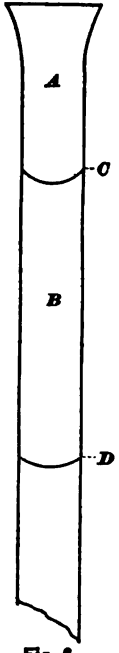

Fig. 6

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used by the writer is a folding boxwood rule; but any rule divided in millimeters will answer the purpose.

4th. A water bath, Fig. 4, made of sheet copper. It is provided with a rack to hold the tubes while being heated, also a feed and overflow (C) to keep the water in the bath at a constant level. In the cut the side is broken away to show the rack and method of supporting the tubes in the bath.

5th. A wash bottle, Fig. 5, to hold hot water.

SOLUTIONS REQUIRED.

The solutions required for the process are as follows:

No. I. 8.75 ounces (250 grams) caustic soda and
10.7 ounces (300 grams) caustic potash dissolved in
4 pounds (1809 grams) water.

Use ten cubic centimeters of the solution for each analysis.

No. II. Equal parts of commercial sulphuric and acetic acids.
The acetic acid should be of 0.047 specific gravity.

Use ten cubic centimeters of the mixed acids for each analysis.

DIRECTIONS FOR ANALYSIS.

Taking Samples.—Mix the milk thoroughly by pouring from one vessel to another, avoiding as much as possible the formation of air bubbles; warming the milk to 80–90° Fah. will prevent frothing to a large extent. After mixing allow the milk to stand one or two minutes, to permit the air bubbles to escape before taking samples. Fill the 20 c. c. pipette, Fig. 2, by placing the lower end in the milk and sucking until the milk rises in the tube above the mark on the side. Place the finger quickly on the top of the tube and allow the milk to run out slowly, until it falls to the mark on the side of the tube; then let the contents of the pipette run into one of the analytical tubes, Fig. 1, blowing out the last few drops.

Adding the Alkali.—Fill one of the 10 cubic centimeter pipettes to the mark on the side, with alkali, and allow the solution to flow into the milk just measured. Place the finger on the top of the tube and shake the tube until the milk and alkali are well mixed. A rubber cot on the finger will protect it from the action of the alkali. Treat all samples in the same way. Place the tubes in the rack, B, in Fig. 4, set

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the rack and tubes in the water bath, Fig. 4, and heat the bath until the water boils; continue boiling for two hours, or until the contents of the tube become homogeneous and of a dark brown color similar to that of sorghum molasses. After the tubes have boiled for one hour remove the rack and tubes from the bath and examine the tubes to see if the contents are well mixed. If a whitish layer of casein and fat is found floating on the surface of the liquid, gently shake and roll the tubes till the contents are well mixed. Return tubes to water bath and boil one hour. The tubes are then ready for the addition of the acid.

Adding the Acid.—Remove the rack with the tubes from the water and allow them to cool to about 150° Fah. Then by means of the pipette, add 10 cubic centimeters of the acid mixture to each tube, slowly, so as not to cause the contents of the tube to froth over. Mix the acid with the contents by running a small glass tube to the bottom of the mixture and blowing gently. Place the rack and tubes again in the bath and heat to boiling for one hour. Remove the tubes from the water and then by means of the water bottle, Fig. 5, fill the tubes with *hot* water to within one inch of the top. The fat will then rise to the top of the water. Replace the tubes in the bath and allow them to stand in the hot water, without boiling, for one hour. At the end of this time remove the tubes from the bath, one at a time, and measure while hot.

Measuring the Fat.—By reference to Fig. 6, the reader will observe that the lines C and D, representing the upper and lower limits of the column of fat, do not extend straight across the tubes; but are slightly curved. In measuring the column of fat, place the rule on the tube so that the line D will come opposite the lowest part of the curved line of the fat, D, Fig. 6; then read up the scale to the division coming opposite the lowest part of the curved line C, Fig. 6. The number of divisions on the rule between C and D, is the length of the column of fat in millimeters. The per cent. of fat in the milk is then calculated from the following formula and data:

Amount of milk taken, 20 cubic centimeters.

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Specific gravity of milk, 1.032.

Specific gravity of insoluble fatty acids, .914.

Per cent. of insoluble fatty acids in butter fat, 87.

From the above data we have the following formula:

$$\text{(No. 1.)} \quad 100\frac{a \times b \times c}{d \times e} = x$$

Where a = the length of the column of fat in millimeters.

b = the value of one linear millimeter of measured fat expressed in cubic centimeters. The value of b will vary, according to the size of the tube used.

c = specific gravity of the insoluble fatty acids.

d = 20.64 grams, or the volume of milk taken for analysis multiplied by its specific gravity.

e = per cent. of insoluble fatty acids in butter fat.

x = per cent. of fat present in sample of milk taken for analysis. Substituting the figures obtained by an actual analysis the formula would be—

$$\text{(No. 2.)} \quad 100\frac{30 \times .027 \times .914}{20.64 \times .87} = x = 4.12$$

Per cent. of fat in sample of milk analyzed.

In practical work the above formulas would be done away with, and one simple factor used instead.

If the process has been conducted according to the above directions the column of fat will be free from impurities and the line of separation between the water and fat will be perfectly clear. On first rising to the surface the fat is slightly turbid owing to the presence of a small quantity of water. Although this will make no appreciable difference in the measurement of the fat, it may if desired be obtained perfectly clear by removing the tubes from the bath and allowing them to cool slowly. The crystalization of the fat causes the finely divided water, which is distributed through the fat, to collect in drops which sink to the bottom when the tubes are again heated, leaving the fat perfectly clear.

The analyst may fail to obtain correct results from the following causes. Either the column of fat may contain flecks of undecomposed casein, which would increase the volume of fat, thereby giving too high a per cent., or a small quantity of

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butter fat may remain unsaponified, which will also give too high results. These errors are both caused by insufficient heating of the milk with the alkali, and may be easily obviated by taking care to heat the mixture of milk and alkali for two hours at least. If not pressed for time it is better to heat two and one-half hours and thereby remove all risks of the above errors. If milk containing more than six per cent. is to be tested, the mixture of milk and alkali should be heated, at least, three hours. In such case it would be better, perhaps, to take ten cubic centimeters in place of the usual amount.

Before adding acid the tubes and contents must be allowed to cool to 150° Fah. at least. If added at a higher temperature, the contact of the strong acid with the hot alkali solution will generate sufficient heat to cause the contents of the tube to boil with explosive violence, throwing out the contents of the tube and spoiling the analysis. If after the addition of hot water the tubes are allowed to stand in boiling water, small bubbles of gas are given off by the continued action of the acid on the casein. These bubbles rise through the column of fat, rendering it turbid and causing difficulty in measuring. The bottles containing the solutions of acid and alkali should be kept corked when not in use. If the acid bottle be left open the acetic acid will evaporate and the acid will not dissolve the casein. The alkali bottle should be kept closed to prevent absorption of carbonic acid and consequent weakening of the solution.

To ascertain the accuracy of this process, duplicate analyses of the same milk have been made both by the regular gravimetric method and the new process. In comparing the results obtained by the two methods we must keep in mind the fact that the new process is intended for commercial analysis and does not claim the extreme accuracy called for in scientific work. The slight variations between the gravimetric and the new method are due to the fact that the data used in calculating the per cent. of fat are the averages of a larger number of milks. From these averages individual milks may vary enough to introduce a small error. This variation, however, is rarely more than two-tenths of one per cent., the usual error

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being no more than by the gravimetric method. With herd milk the difference between the two methods would be less than in the analyses given below, as these are almost all from the milk of individual cows. Owing to the individual differences that exist in the milk of single cows the analysis of such milks is the severest test to which a new process can be put. Following is a list of the cows whose milk has been analyzed separately :

Name of Cow.	Breed	Calved.
Topsy	Half Blood Holstein	October, 1887.
Palmer	Grade Short Horn	September, 1887
Sylvia	High Grade Jersey	October 3, 1887.
Bessie	Grade Jersey	Jan. 12, 1888.
Rose	Grade Jersey	October, 1887.
Cowry	Full Blood Jersey . . . Last Calf	Nov., 1884.
Mattie	Half Blood Holstein	Oct. 3, 1887.
Purcell	Native	Fall, 1887.
Rusk	Grade Jersey	Jan. 24, 1888.
Doubtful 2nd	Grade Jersey	Dec. 29, 1887.
Daisy 2nd	Grade Jersey	
Roan	Grade Short-horn	April 14, 1887.
Gipsy	Grade Short-horn	September, 1887
Jessie	Grade Jersey	Fall, 1887
Sylvia 2nd	Grade Jersey	Jan. 27, 1888.
Hopsie	Full Blood Holstein	Owned by E D. Frost, Almond, Wis.
Hammeka	Full Blood Holstein	

Several samples of milk from pure blood Holsteins were sent to the Station by Mr. E. D. Frost. Mr. J. A. Smith, of Saukville, also contributed samples of factory milk.

Samples of the morning's milk from each of the above cows, except the last two, were brought each morning to the laboratory and immediately weighed out for gravimetric analysis; at the same time the milk was analyzed by the new process, two or more duplicates being measured out and the analysis finished within three hours. The following table gives the results of 41 milks analyzed in this manner.

The gravimetric method used is the same as that given by Dr. Babcock in Report of the New York Agl. Exp. Station, 1883, p. 167.

The following table gives the comparative results obtained by the writer with the gravimetric and new methods :

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No.	Name of Cow.	Method.		Date.	Remarks.
		Short's.	Gravimetric.		
1	Topsy	4.46	4.47	Dec. 20, 1887.	
2	Topsy	4.33	4 47	Dec. 21, 1887.	
3	Topsy	4.47	4.38	Dec. 22, 1887.	
4	Palmer	4.87	4.73	Dec. 22, 1887.	
5	Topsy	4.47	4.66	Dec. 20, 1887.	
6	Palmer	5.64	5.58	Dec. 24, 1887.	
7	Palmer	4 75	4.70	Dec. 26, 1887.	
8	Topsy	4.50	4.60	Dec. 26, 1887.	
9	Palmer	5.02	5 04	Jan. 2, 1888.	
10	Sylvia	5.90	5.92	Jan. 4, 1888.	
11	Bessie	4 55	4.68	Jan. 4, 1888.	Colostrum milk.
12	Rose	3.74	3.63	. . . . .	
13	Cowry	8.91	8.97	. . . . .	From stripper.
14	Rose	3.22	3.23	Feb. 11, 1888.	
15	Mattie	2.61	2 75	Feb. 11, 1888.	
16	Cowry	6.96	7.23	Feb. 13, 1888.	From stripper.
17	Purcell	3.96	3.99	Feb. 13, 1888.	
18	Mattie	2.75	2.95	Feb. 14, 1888.	
19	Rusk	3.86	3.99	Feb. 15, 1888.	
20	Doubtful 2nd .	3.31	3 55	Feb. 16, 1888.	
21	Cowry	7.29	7.48	Feb. 16, 1888	
22	Daisy 2nd	4.27	4.46	Feb. 16, 1888.	
23	Roan	4.51	4.52	Feb. 17, 1888.	
24	Gipsy . . .	3.64	3 84	Feb. 17, 1888	
25	Cowry	7.30	7.37	Feb. 17, 1888.	
26	Sylvia	5.90	5.75	Mar. 13, 1888.	
27	Jessie	4 83	4.79	Mar. 14, 1888.	
28	Daisy 2nd . . .	5.27	5.05	Mar. 15, 1888.	
29	Sylvia	4.55	4.77	Mar 16, 1888.	
30	Jessie	4.57	4.75	Mar. 17, 1888.	
31	Herd	2.77	2.85	. . . . .	
32	Herd	2.26	2.32	. . . . .	Above milk partly skimmed.
33	Herd	4 16	4 11	. . . . .	
34	Herd	2.11	2 17	. . . . .	Above milk partly skimmed.
35	Herd	1.78	1.84	. . . . .	Skimmed 2d time.
36	Factory milk .	3.50	3 47	. . . . .	From J. A. Smith, Saukville, Wis
37	Factory milk .	3 80	3.64	. . . . .	
38	Factory milk .	2.90	2.86	. . . . .	
39	Herd	3.41	3.49	. . . . .	Sent by E. D. Frost, Almond, Wis
40	Hopsie	3.83	3.75	. . . . .	
41	Hammeka . .	3.98	3 75	. . . . .	

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In order to determine if previous laboratory training is necessary to conduct analyses by this method, Mr. L. H. Adams, the farm superintendent, who has had no experience in chemical work, was given the apparatus with printed directions and made the following analyses without further instructions, the writer at the same time making gravimetric determinations of the same milk with the following results:

Analyzed by Adams.		Analyzed by Short.	Date.	Milk.
No.	Short's Method.	Gravimetric.		
1	4.69	4.74	Feb. 21, 1888.	Mixed milk.
2	4.33	4.18	Feb. 21, 1888.	Mixed milk.
3	4.18	4.25	. . . . .	Mixed milk.
4	4.01	4.17	Feb. 22, 1888.	Mixed milk.
5	4.77	4.62	Feb. 23, 1888.	Mixed milk.
6	4.22	4.37	Feb. 23, 1888.	Mixed milk.
7	3.77	3.67	Feb. 24, 1888.	Mixed milk.
8	4.25	4.17	Feb. 24, 1888.	Mixed milk.
9	7.42	7.63	Feb. 25, 1888.	Mixed milk.
10	3.58	3.56	Feb. 25, 1888.	Mixed milk.
11	3.29	3.28	Feb. 25, 1888.	Mixed milk.
12	4.56	4.45	Feb. 25, 1888.	Mixed milk.
Average	4.422	4.423	. . . . .	. . .

To give the method still further trial, Dr. Babcock conducted gravimetric analyses while two students pursuing agricultural studies, analyzed the same samples by the new method. Neither of the students had had any training in laboratory work.

Printed instructions were given them as in the case of Mr. Adams; and they received no further aid. The students went through the several steps of the process once in order to familiarize themselves with it, before making the analyses given below:

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Analyzed by Students.			Analyzed by Dr. Babcock.		Student.
No.	Milk.	Short's Method.	Gravimetric.	Date.	
1	Herd milk.	4.08	4.13	Mar. 3, '88.	C. D. Wolfram.
2	Herd milk.	4.00	4.00	Mar. 4, '88.	C. D Wolfram.
3	Herd milk.	3.73	3.72	Mar. 5, '88.	G. A. Carswell.
4	Herd milk.	3.70	3 71	Mar. 5, '88.	G. A. Carswell.
5	Herd milk.	4.56	3.76	Mar. 6, '88.	G. A. Carswell.
6	Herd milk.	4 26 (?)	4.63	Mar. 6, '88.	G. A. Carswell.
7	Herd milk.	4.29	4.48	Mar. 6, '88.	G. A. Carswell.
8	Herd milk.	4.01	4.07	Mar. 7, '88.	G. A. Carswell.
9	Herd milk.	4.13	4.35	Mar. 7, '88.	G. A. Carswell.
10	Herd milk.	4.41	4.30	Mar. 7, '88.	G. A. Carswell.
	Average .	4.11	4.22		

In order to further test the method in hands of other parties and with different kinds of milk, complete sets of apparatus were sent to Mr. E. F. Ladd, chemist of the New York Agricultural Experiment Station, and to W. J. Ives, State Dairy Commissioner of Minnesota. These gentlemen were kind enough to make comparisons of the process with the regular gravimetric method. Mr. Ladd writes under date of May 20th, 1888, as follows:

I have carefully tested the method worked out by Mr. Short for the determination of fat in milk, using the apparatus furnished by you. Below I give you the results of my several trials by the method, in comparison with gravimetric analyses:

Per Cent. of Fat in Milk.

No.	Gravimetric	Short's Method.
1	5 03	4 99
2	4.62	4.71 4.74 4.71
3	4.60	4.60
4	5.00	5.16 5.19
5	5.69	5.84 5.86
6	5.13	5.22
7	4 88	4.88
8	6.95	6.97 7.10
9	6.77	6.76
10	4.57	4.52

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Nos. 2 and 5 were the mixed milk from several cows. Other determinations were with the milk of individual cows.

I have tried several of the methods prepared for the estimation of fat in milk without success. The Lactobutyrometer method generally recommended as the best, has nearly always proved very unsatisfactory with the milk from the Station dairy.

I consider Mr. Short's method the most reliable of any yet offered as a substitute for gravimetric analysis of milk.

(Signed) Very truly yours,
E. F. LADD."

The apparatus sent to W. J. Ives was tested by W. S. Eberman, chemist of the Dairy Department. The first analyses made by him are as follows:

Per Cent. of Fat in Milk.

No.	Gravimetric	Short's Method.
1	3.50	3.38
2	3 80	3.31
3	3.60	3.36
4	3.40	2 29
5	4 00	3.61

A second set of analyses made by Mr. Eberman gave the following results:

Per Cent. of Fat in Milk.

No.	Gravimetric.	Short's Method.
1	3 60	3.74
2	2 90	3 36
3	3 70	3.93
4	4.20	4.28
5	4 00	3 91

The method of gravimetric analysis used by Mr. Eberman was that of Wanklyn as modified by Davenport. Its essential points are drying the milk, in a platinum dish, over a water bath; and the extraction of the dried residue with petroleum ether. It is a well-known fact that Wanklyn's process almost invariably gives a lower per cent. of fat and the results are less

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uniform than those obtained by continuous extraction of the dried residue with ether. This fact is sufficient to explain the differences between the two methods shown in the above table.

CREAM.

The above process can be used for the analysis of cream by taking the following precautions : See that the cream is perfectly sweet and well mixed, then by means of a suitable vessel measure out one part of cream and two parts of water. Mix the cream and water by pouring from one vessel to another as in sampling milk. Take the sample immediately before the mixture of cream and water has had time to separate. Continue the analysis in the same way as for milk, and to calculate results make use of the following formula and data :

Amount of diluted cream taken, 20 cubic centimeters. Specific gravity of diluted cream 1.000 or the same as water. Specific gravity of insoluble fatty acids, .914. Per cent. of insoluble fatty acids in butter fat, 87. The above data gives us the following formula :

$$100\frac{a \times b \times c}{d \times e} = x$$

Where a = the length of the column of fat in 15 millimeters.

b = the value of one linear millimeter of measured fat expressed in cubic centimeters. The value of b will vary according to the size of the tube used.

c = specific gravity of the insoluble fatty acids.

d = 20.00 grams, or the volume of diluted cream taken for analysis, multiplied by its specific gravity. Assuming that the specific gravity of the diluted cream is the same as that of water, or 1,000. e = per cent. of insoluble fatty acids in butter fat. As the cream is diluted with twice its weight of water, the result obtained by the above formula should be multiplied by three to find the per cent. of fat in the normal cream.

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It is not claimed that this method gives accurate results with milk containing under one-half per cent. of fat, although it will show any watering or skimming of the milk down to that point. Milk from which all but a fraction of a per cent. of the fat has been removed, possesses certain peculiarities which we are unable to explain. As a result of this no method yet devised, with the exception of the regular gravimetric analysis, will show the amount of fat, in milk containing under one-half per cent. of fat. Whether this peculiarity is due to a difference in the composition of the small fat globules remaining in the milk or to some physical change in the milk itself, is at present unknown. Further investigations may find a way to overcome this difficulty; but at present, without the use of minute precautions which would be impracticable in commercial work, there is no practical method for determining the amount of fat in skim milk containing less than one-half per cent. of fat.

NOTE BY DR. WILEY.—The method of Short has been compared in my laboratory with the anhydrous method of Piggott & Morse. A mean of 12 determinations gave by the anhydrous copper method 3.20 per cent. of fat and by the Short method 3.18 fat. The same samples treated by the Adams method gave results considerably higher. The process of Short has also been improved by graduating the neck of the tube into tenths of a cubic centimeter.

For use at stations where expensive chemical apparatus cannot be had the method appears to have great value.

[Communications from the Laboratory of Cornell University. IV.]

RAPID DETERMINATION OF N_2O_5 IN NITRATES.

BY FRANK H. MORGAN AND EDES BATES.

Of the many modifications of the Pelouze method of determining N_2O_5 by its oxidizing action on a ferrous salt, Fresenius recommends as best the following.*

Air is removed and excluded from the apparatus by a current of CO_2; into the flask containing the nitrate, a solution of $FeSO_4$ in strong HCl is passed, and after an interval ("noch eine zeit lang") the contents of the flask are warmed for some time ("zwar anfangs längere Zeit ganz gelinde")

*Anleitung zur Quant. Anal., 6 ed., I, 521.

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and finally heated *gradually* to boiling. When the action is complete and all nitric oxide swept out of the flask, its contents are diluted with a double volume of water and the ferric iron determined by running in a slight excess of $Sn\ Cl_2$, cooling, and titrating the excess of $Sn\ Cl_2$ by iodine.

This method, with care, will yield good results, but it requires from an hour and a half to two hours for a single determination, after the four necessary solutions are prepared and standardized.

The writer has endeavored to improve this process in the following points.

1. By reducing the number of solutions required from four to two, or practically to one. This has been accomplished by the use of an accurately standardized solution of $FeCl_3$ (in HCl), which, by reduction with $SnCl_2$ solution, furnishes the $Fe\ Cl_2$ for the reduction of the nitrate, and at the same time measures the strength of the $SnCl_2$ solution.

2. By shortening the time of the reaction between the $Fe\ Cl_2$ and N_2O_5.

This has been accomplished by bringing the nitrate into the strongly acid ferrous solution, at a temperature near to boiling (80° to 90° C.)

3. By securing an exact end point in the reduction of the ferric salt by $Sn\ Cl_2$, and doing away with the subsequent titration by iodine.

Accomplished by use of the "*blue flame indicator*" * described in a previous paper.

4. The attainment of the preceding has developed the most important improvement, by making it possible to carry on a number of consecutive determinations in the same flask and solution, without allowing apparatus or solution to cool; the number being limited only by the gradual saturation of the liquid with the salts formed in the reaction.

The details of the method based upon the preceding points are as follows:

I. Apparatus. See Fig. 1.

* This Journal, II, p. 169.

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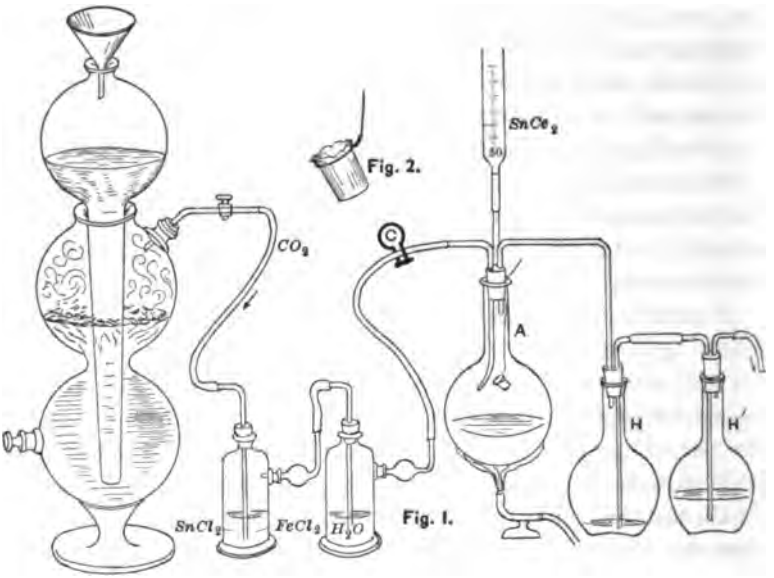

A Kipp's generator and wash bottles for production of pure CO_2. A 400 c. c. r. b. flask A, with tubes for entrance of CO_2, and exit of products of the reaction, through the guard flasks H and H_1. The latter are so arranged as to prevent access of air to flask A, from any momentary cooling of its contents.

II. Reagents.

$Fe\,Cl_3$ solution, (1 c. c. = about .025 grms. Fe''') carefully prepared free from any Fe'' or oxidizing agents, and strongly acid with HCl. $SnCl_2$ solution (a) or (b) according as one uses gravimetric or volumetric measurements.

(a) Pure Sn 75 grms; HCl (1.2) 300 c. c.; H_2O to 1000 c. c.

(b) Pure Sn 25 grms; HCl (1.2) 300 c. c.; H_2O to 1000 c. c.

III. Operation of analyses.

Measure 50 c. c. (or 50 grms.) of $Fe\,Cl_3$ solution, and pour into flask A; rinse in with 25 c. c. of HCl and 25 c. c. H_2O; boil for five minutes, with a current of pure CO_2 passing; remove the CO_2 tube from cork in flask A, while the solution is kept boiling, and thrust into its place the jet of the $SnCl_2$

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burette. Run $Sn\ Cl_2$ from the burette rapidly at first, more gradually as the blue flame seen through the solution indicates the approach of saturation; finally drop by drop, regulating the heat so that the solution boils gently, until the last trace of green disappears from the flame, indicating the completion of the reduction. The burette is now again replaced by the CO_2 tube and the lamp removed. We have now in the flask $Fe\ Cl_2$ for the subsequent reduction of the N_2O_5, and we know the strength of the $Sn\ Cl_2$ solution in terms of Fe'''.

N. B—As two tests of the strength of the $SnCl_2$ are desirable, the above may be repeated; or better, performed first on 25 c. c. of $FeCl_2$ and then on 25 c. c. more, having care to boil this portion five minutes outside and then to pour slowly into flask A, under protection of a rapid current of CO_2 and a gently boiling solution.

The nitrate having been weighed in a small shallow tube (see Fig. 2), the cork in flask A is lifted (CO_2 running rapidly) and the nitrate suspended by a fine platinum wire, in such a position that it is in the current of CO_2; after 3 minutes, by raising the cork slightly, the platinum wire slips through, dropping the nitrate tube into the solution where, aided by a gentle rotatory motion of the flask, it at once enters into rapid reaction with the hot strongly acid $FeCl_2$.

After two minutes, put a small flame under the flask, and bring to a boil in five minutes. Boil vigorously for ten minutes longer, during which time the clamp C should be shut, to prevent any NO from being forced over to bottle W′.

The solution should now be a clear, red brown, and is ready to titrate*.

Remove the CO_2 tube, insert the burette and reduce the solution by the $SnCl_2$ as in the preliminary titration; the amount of $SnCl_2$ used is of course a measure of the amount of nitrate that has reacted on the $FeCl_2$.

A second determination is now carried on as follows: The burette being removed, the cork D is raised, the flask inclined, and the nitrate tube removed by means of a platinum or glass hook; 25 to 35 c. c. of HCl (conc.) and 10 to 20 of water are

* It is well to test the gas escaping at H′ by a solution of KI and starch as recommended by Fresenius loc. cit. p. 521.

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added (sufficient to bring the volume to original amount), the cork inserted and the contents of the flask boiled three minutes (CO_2 running).

If any oxidation is apparent, it is carefully reduced by $SnCl_2$ from the burette ; one or two drops generally suffice.

Another portion of nitrate may now be inserted, and the previous operation repeated.

The accuracy and rapidity of consecutive determinations in the same solution is shown by the following series of seven determinations of N_2O_5 in ordinary C. P. KNO_3, using gravimetric measurement of solutions in the Burette flask.*

$FeCl_3$ sol. 1 grm. equiv. to .02492 Fe'''.

Preliminary titration of $SnCl_2$, and formation of $FeCl_3$.

	$FeCl_3$ Sol.	*$SnCl_2$ required.*	*1gm. $SnCl_2$ equivalent.*
(a)	56.065 gms.	17.741 gms.	.07874 gms. Fe'''
(b)	56.001 "	17.749 "	.07865 " "

Hence 1 grm. $SnCl_2$ equiv. to .07869 grms. Fe'''.

Assays of KNO_3 (marked C. P.)

No.	*Subst. taken.*	*$SnCl_2$ used.*	*N_2O_5 equiv.*	*Per cent. N_2O_5*
1	.5254 grm.	11.005 grm.	.2784 grm.	52.98 per cent.
2	.5324 "	11.148 "	.2819 "	52.95 "
3	.5134 "	10.763 "	.2723 "	53.04 "
4	.5267 "	11.019 "	.2787 "	52.91 "
5	.5176 "	10.828 "	.2738 "	52.90 "
6	.5134 "	10.756 "	.2720 "	53.01 "
7	.5071 "	10.673 "	.2692 "	53.08 "

NOTES.—Average time for a single assay was 30 minutes; temperature of the solution at time KNO_3 was inserted was 80° to 90° C.

When the HCl was added, previous to the 6th assay, a slight precipitation of a crystalline salt took place; this redissolved quickly on boiling.

After the 7th assay, as the liquid became cold, a considerable amount of crystalline substance separated.

The following analyses were made by Mr. Eads Bates, at the time a student of one year's experience in quantitative work. The solution of $FeCl_3$ used was the same as in the preceding; the $SnCl_2$ was a weaker solution, measured from an ordinary burette.

*This Journal II., 1.

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Preliminary titrations.

	$FeCl_3$	*$SnCl_2$ required.*	*1 c. c. $SnCl_2$=Fe'''*
(a)	36.973 grms.	40.59 c. c.	.02269 grms. Fe'''
(b)	45.652 "	50.10 "	.02271 " "

Assays of KNO_3 (marked C. P.)

No.	*Subst. taken.*	*$SnCl_2$ used.*	*N_2O_5 equiv.*	*N_2O_5 per cent.*
1	.5835 grm.	42.30 c. c.	.3086 grm.	52.88 per cent.
2	.5241 "	38.00 "	.2773 "	52.90 "
3	.4622 "	33.60 "	.2444 "	52.88 "
4	.3499 "	25.50 "	.1861 "	53.18 "

The results already obtained proving that the method was relatively accurate, some of the same nitrate was carefully purified by recrystallization and drying at 150° C. and analyzed by the same process.

Six analyses in series, gave the following results, obtained by rapid work, without extraordinary care.

	Obtained.	*Theoretical.*	*Differences.*
	53.27 % N_2O_5	53.41 % N_2O_5	—0.14 % N_2O_5
	53.38 "	53.41 "	—0.03 "
	53.33 "	53.41 "	—0.08 "
	53.50 "	53.41 "	+0.09 "
	53.50 "	53.41 "	+0.09 "
	53.31 "	53.41 "	—0.10 "
averg.	53.38 "	53.41 "	—0.03 "

Remarks.

1. Some experiments were made to determine the best conditions for rapidity and completeness of the reactions. The results obtained show that the nitrate should be introduced in the solid form or in a very concentrated solution, otherwise the reaction (decomposition of the N_2O_5) is very slow, and abnormal reactions may take place.

Introducing the nitrate in solution (.5 grm. in 25 c. c.) and proceeding as above, the reduction by $SnCl_2$ was followed by

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immediate and continued recurrence of the yellow color, necessitating successive additions of $SnCl_2$, which if continued to a permanent colorless point gave results from one to ten per cent. high. This difficulty (not due to imperfect exclusion of air) arises from the presence of undecomposed nitrate ; when $SnCl_2$ (containing HCl) is run in, more nitrate decomposes and abnormal reactions are possible between the $SnCl_2$ and the nitric oxide which is set free.*

2. The perfect exclusion of the air can only be easily secured by a current of pure CO_2, which proved to be much better than hydrogen.†

With the time of an analysis made very short, as by the above process, the possibility of error from this source is greatly reduced and the elaborate precautions given by Warington are unnecessary.

3. $CoCl_2$ (HCl) was also tried as an indicator, but proved impracticable for a series of consecutive determinations, on account of the greenish yellow color that the solution acquires after two or three titrations with $SnCl_2$. This color is not strong enough to vitiate the "blue flame" end point, and any slight error of excess of $SnCl_2$ before an analysis is compensated by a possible similar error at the end.

ANALYTICAL LABORATORY, CORNELL UNIVERSITY.

USE OF HYDROGEN PEROXIDE IN ANALYSIS.

BY F. P. DUNNINGTON.

Lead peroxide may be most readily dissolved by treatment with dilute nitric acid and a solution of hydrogen peroxide. Half of the oxygen from each of the two peroxides unite to produce an effervescence of oxygen, even when cold, resulting in the formation of a solution of lead nitrate.

* See Dives and Haga, J. Chem. Soc. **47**, 623.

† Warington, J. Chem, Soc. **41**. 346; also Ztschr. anal. chem. **23**, 548, gives very good directions for securing pure CO_2.

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A similar action of hydrogen peroxide, I have frequently found of advantage in effecting the solution of a precipitate produced by ammonia and consisting mainly of ferric and alumina hydrates, in which however, after washing, a little manganese is retained as Mn_2O_3. The latter body will resist solution in dilute acid, and under these circumstances a drop or two of hydrogen peroxide will instantly clear up the solution.

In the same manner, ignited oxide of cerium or oxide of manganese may be readily dissolved by cold dilute acids mixed with hydrogen peroxide.

UNIVERSITY OF VIRGINIA, September 10, 1888.

SOME LECTURE EXPERIMENTS.

BY EDWARD HART.

(1) PREPARATION OF GASEOUS AMMONIA.

The preparation of gaseous ammonia for lecture purposes is always attended with difficulty unless, as Hofmann recommends, a reservoir of liquified gas be kept on hand. This is not always convenient or possible, and I have recently hit upon the following method, which is extremely easy to carry out and which gives an abundant yield of pure and tolerably dry gas. A half liter flask is filled half full of pieces of stick caustic potash and strong aqua ammonia is run into the flask drop by drop. The caustic potash dissolves in the water and the ammonia is given off very rapidly. So much heat is absorbed by the gasification of the ammonia that the liquid becomes very cold and this insures the dryness of the gas given off. If desired the solution of caustic potash can be boiled down and used over again.

(2) PREPARATION OF ETHYLENE DICHLORIDE.

One of the most interesting properties of olefiant gas, and

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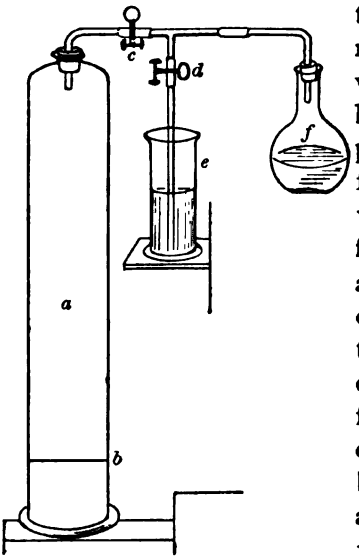
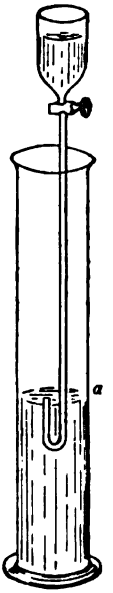


the one to which it owes its name, is the property of uniting with chlorine gas, forming Dutch liquid. This experiment is best performed on the lecture table as follows: The cylinder *a* is filled with water and then to *b* with olefiant gas. Chlorine gas is generated in the flask *f* from manganese dioxide and hydrochloric acid and the gas allowed to bubble through caustic soda solution in *e* until free from air, when *d* is closed and *c* opened. The chlorine then combines with the olefiant gas in *a* and forms ethylene dichloride which floats upon the surface of the water. When enough chlorine has been added *c* is closed and *d* again opened.

(3) DETECTION OF NITRIC ACID.



The familiar method of detecting nitric acid by means of the dark ring formed at the junction with a ferrous sulphate solution may be shown to a large audience as follows: The jar *a* has a diameter of 2 inches and any convenient height. This is half filled with the soluiion of the nitrate properly acidified and the ferrous solution is poured on it by means of the funnel tube with turned up end. In this way danger of mixing the two liquids is avoided. If the amount of nitric acid is small it is necessary to wait some time before the colored ring makes its appearance. In order that this may be clearly seen a sheet of white paper or card should be placed below and another behind the cylinder.

(4) THE CLARIFYING ACTION OF ALUM UPON MUDDY WATER.

Filters in which alum in minute amounts is added

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to the water before filtration have been introduced of late years in a great many places and have proved very valuable as a cheap and efficient means of securing pure clean drinking water. Where they are in use for city or town supply the deadly private filter can be thrown aside. That a small quantity of alum added to muddy water does actually coagulate the suspended mud can be readily shown as follows: Some muddy water is placed in each of two tall wide cylinders to one of which a few grains of alum in solution is added. The contents of both cylinders are then filtered through separate paper filters and the filtrates collected separately. The water to which the alum has been added will be perfectly clear and bright after filtration while the other will still contain suspended matter.

[Communications from the Laboratory of Cornell University. V.]

PROGRESS IN CHEMICAL METHODS OF SANITARY WATER ANALYSIS.

By Frank H. Morgan.*

A review of recent investigations relating to methods of analysis of potable waters shows a gratifying increase of interest in the problem of determining the fitness of a water for drinking purposes.

Counting from Forchammer's introduction of the use of permanganate, chemists have worked at this problem for forty years. How little satisfactory progress has been made is illustrated by the general conclusions of Prof. Mallet drawn from the results of the comprehensive investigation so admirably conducted by him for the U. S. Board of Health.†

He says, "it is not possible to decide absolutely upon the wholesomeness or unwholesomeness of a drinking water by the mere use of any of the processes examined for the estima-

* A paper read before the chemical section of the A. A. A. S. at the Cleveland meeting with some changes by the author.

† Ann. Rept. Nat. Board of Health (U. S.), 1882, p. 207.

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tion of *organic matter* or its constituents." Consideration of this slow progress of forty years ought to convince us of the inadequacy of purely chemical methods (or chemists !) alone, for the resolution of conditions resulting from, or intimately related to biological as well as chemical changes. Hueppe* introduces the consideration of bacteriological examination of water by the following incisive and significant remark (the italics are introduced by the writer): "The chemical investigation of water *alone* can furnish *no information* as to *hygienic fitness* or unfitness of a certain water for use and drinking."

Farther on (next page) he concludes the consideration of chemical methods as follows: "With freedom from its limitations and careful consideration as to local conditions, now as formerly, *valuable conclusions* may be drawn as to the *hygienic value* from the usual chemical examination."

While a chemist may rightly protest against the absolute denial of the first, and call attention to the incompatibility of the two statements, it is perhaps wiser to accept the evident animus of the whole as a just and proper diagnosis.

In undertaking to determine the potability of a water the chemist becomes a sanitarian and must have all obtainable evidence as to source, past history, etc., in order to properly interpret the purely chemical evidence.

As chemists we should not pretend to the determination of hygienic value, strictly speaking.†

We must confine ourselves to the resolution of the chemical condition of a water and the character of its chemical constituents. With this aim, studies of the relations of the chemical character of a water to the biological influences to which its constituents have been subjected in the past, become legitimate chemical research. Therefore, while there seems to be some necessity for changing our attitude toward this question,

* "Methods of Bacteriological Investigation," (Bigg's Translation) p. 202.

† An interesting discussion has recently arisen in England in regard to the closure of polluted wells; the law insisting on testimony that the water is *injurious* to health; conscientious chemists refusing to say more than that it is *dangerous*.

† Analyst **13**, p. 141 (August, 1888).

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all must admit (as does Hueppe above) the very practical value of the chemical examination. The urgency of continued study and improvement in chemical methods has then a sound basis, and is decidedly emphasized by the present impracticable state of biological methods when unassisted chemically.

In the hope of inciting others to work in this field, a careful study of the literature of sanitary water analysis by the writer is perhaps a sufficient ground for offering the following summary of important lines of enquiry now demanding attention in this field:

I.—*A careful bibliographical review of the work of the past forty years on all methods of examination of potable waters. A complete index of the literature and carefully drawn monographs of each method that has been in general use.**

The need of such work and the benefits that would accrue are apparent to all interested.

Much desultory work now being done because of a lack of appreciation of that which has been done; the pursuit of minor details long ago worked out; the announcement of new precautions here and there which are only tolerated as original because forgotten, would be done away with. A truer conception of the direction of real progress would follow. The excellent critical review of methods in Mallet's † report, while very useful, emphasizes in the mind of the student of this subject the need of more complete work of a similar kind.

II.—*A careful regulation and adoption of uniform methods of procedure for those processes at present in general use.*

The results obtained by these processes being relative rather than absolute chemical quantities, uniform and constant conditions are necessary to render the work of different chemists comparable, and thus afford a fund of experience valuable for all. Such regulation can best be attained as a sequel to the accomplishment of the preceding suggestion (I). ‡

* The writer is now at work on such an index and monograph of the "ammonia process."

† Loc. cit., p. 217.

‡ In this connection the chemical section (A. A. A. S.) were urged to under-

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III.—*Careful investigations of modifications of the "ammonia" and "oxygen" processes for the purpose of securing more definite results as to the amount and character of the organic matter.*

Recent investigations have been very suggestive in this direction, and some work already done by Mallet * Smart ** Drown *** and others suggested the opening remark in this paper.

Dr. Leeds † after an ineffectual attempt to accurately determine the total organic nitrogen and carbon of known substances by wet processes, abandoned the field. There are, however, some possibilities yet untried and others should not be deterred from further work in this direction. While a knowledge of the gross amount of organic nitrogen and carbon may have little hygienic significance it would form an important basis for studies of chemical character. The writer believes that the ammonia process may be made to render more significant results by modifications to be described later on.

IV.—*Careful studies of the conditions of nitrification in the soil and in water; or more broadly, of the relations of chemical character to biological species and their activity.*

Admitting, as above, that purely chemical researches are inadequate for determination of hygienic value of a water it seems probable that (chemically unaided) biological methods will ever remain impracticable for general use. Cannot the chemist, with the biologist's aid, determine the chemical equation of specific micro-organisms?

The work of Schlœsing and Müntz, and of Warrington is

take a consideration of *methods of procedure* in water analysis as paramount in importance to *methods of stating results.* Later, the section instructed the committee already appointed, to consider and recommend methods of procedure for the determination of organic matter.

* Loc. cit. supplementary investigation; **, with Mallet, loc. cit.; *** Technology Quarterly (Boston) 1, p. 250.

† J. Am. Chem. Soc. 9, 162.

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well known. Recent papers by Munro,* Gayon, and Dupetit,** Frankland,*** and others, are evidence of a rich harvest in the near future.

From the biologist's point of view Klein (J. Chem. Soc. *49*, 197) calls attention to the exceeding great care and absolute completeness of the chain of evidence necessary to secure reliable results in the above work.

There is a great need of parallel chemical and biological studies of natural waters throughout the changes of the seasons. In surface waters, the influence of algæ fungi and infusoriæ, even less studied at present than bacteria, have undoubtedly an intimate relation to the chemical condition of the water.

Gerardin † found a definite agreement between the variations of dissolved oxygen and the appearance of certain low forms of vegetable life. Dr. Leeds ‡ also gives much information on this point.

The writer cannot refrain from the suggestion that some of our newly organized agricultural experiment stations might well enter this field; with a botanist and a chemist much good work could be accomplished.

V.—*Trials of new reagents as means of distinguishing different conditions or classes of organic bodies.*

It seems strange that only one reagent is in general use. Besides permanganate several others have been used to a slight extent, but there has been as yet no extended investigation of the quality or character of the organic matter acted upon by these reagents.

Burghardt § announced a partly classificatory method (use of CrO_3 and H_2SO_4), which needs, however, more investigation before judgment can be passed upon it. Griess ‖ pro-

* J. Chem. Soc. **49**, 632; Chem. News **56**, 62. ** Abs. J. Chem. Soc. **50**, 823.
*** J. Chem. Soc. **53**, 373.
† C. R. **80**, 1326; **81**, 989.
‡ J. Franklin Inst., **105**, 193, 241.
§ Chem. News **53**, 271; **55**, 121.
‖ Ber. **21**, 1830.

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poses the use of certain diazo-compounds. The writer proposes to investigate the indications afforded by iodine.*

Dreyfus † investigated the rate of action of $KMnO_4$ on many substances. He found that the action on hydro carbons, sugars, paraffine alcohols and on acids of acetic and benzoic series was quite slow; the action on the aldehyde function was more rapid than on the alcoholic; on the phenols more rapid than on either of these.

Kingzett ‡ intimates that putrescent organic matter does not absorb as much $KMnO_4$ as fresh material, and argues therefrom the indefiniteness of the oxygen processes. The work done in the Mallet investigation will repay a careful study on this point.

VI.—*Studies of the effect of variations in the time, temperature, concentration and pressure on the action of reagents.*

With this work may also be included the influence of those salts generally present in potable waters.

Wigner and Harland § and more recently Dupré's, || have studied the action of $KMnO_4$ under variations of temperature and time. Much more extended work of this kind is necessary before any very significant or definite results can be derived from the present oxygen processes.

Mr. Wanklyn in 1877¶ criticised those methods (Frankland's, etc.) which "search the residue for perishable organic matter which originally existed in the water," and added "in the ammonia process we attack the organic matter in presence of the water, etc." It seems that we might in turn criticise those processes which attack the organic matter at a boiling temperature. The suggestion follows that we look for reagents and methods which shall be applied at ordinary temperatures, in fact with as little change in the physical condition

* See Proceedings A. A. A. S., **37**.

† Compte. Rend. **105**, 523; "abstract" J. Chem. Soc. 24.

‡ J. Chem. Soc. **37**, 15.

§ Analyst. VI, No. 60, p. 39.

|| Analyst, 1882.

¶ Chem. News **36**, 42.

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of the water as possible. As Tidy, Mallet and others have suggested, rate and quality of action may show some relations which gross quantity will fail to do.

SOME NOTES ON RECENT WORK BY THE WRITER.

The following brief resume of work which has included quite a large number of experiments is given, not because of satisfactory results reached, but as a means of emphasizing certain points in the ammonia process.

A. The relative amount of ammonia (as compared with the regular process) developed by the action of a constant quantity of concentrated alkaline permanganate on a constant volume of water.

These conditions were attained by passing the water to be examined (by means of a siphon or funnel tube with glass stopcock) into a flask, containing about 30 c. c. of boiling permanganate, at such a rate (about 1 c. c. per minute) that the ingress just equaled the distillation.

This is in a sense the reverse of the suggestion of Prof. Mallett,* who would keep the volume of water constant by running in ammonia free water, loc. cit. p. 210.

B. Another set of experiments was made to ascertain the effect (on the ammonia produced) of a preliminary treatment with sulphuric acid.

The apparatus in both the preceding enquiries, consisted of long-necked distilling bulbs, with a rubber stopper through which passed a nearly capillary tube extending below the surface of the liquid in the flask. Many irregularities in the results, vitiating their value, were finally traced to the presence of the corks. Both lines of enquiry will be resumed when suitable apparatus can be procured.

Leeds † demonstrated that the use of rubber corks should be avoided in all ammonia distillations. I have mentioned this

* E. Waller in J. Am. Chem. Soc. 8, 150, announced that he was experimenting on "some application of Kjeldahl's method to water analysis," but he has as yet published no results.

† Ztschr. anal. Chem. 18, 428.

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point, as I believe some chemists are in the habit of operating the ammonia process in flasks with the necks corked.

C. On the amount of ammonia developed from the organic matter by the action of the Na_2CO_3 and boiling temperature in the ordinary "free ammonia" determination.

Among the early objections raised against the ammonia process was the fact that ammonia might be developed from certain kinds of organic matter by heating their solution with sodium carbonate; and that therefore the so-called *free* ammonia was indefinite and the term a misnomer.

In defence of his method, Wanklyn * claimed that the steady or continuous evolution of NH_3 by the action of Na_2CO_3 on *urea*, served to distinguish it from ammonia salts in the ordinary distillation.†

It seems possible that something new might be learned from a study of this action of sodium carbonate, as undoubtedly there is some action on other substances than urea. Comparisons of the amount of *free* ammonia by the ordinary distillation and that obtained by direct application of the Nessler's reagent at ordinary temperature, will distinguish the actual inorganic ammonia (NH_4) from the organic ammonia which has heretofore been included in the so-called *free* ammonia.

The application of Nessler's reagent without previous distillation is a very simple operation, yet it requires considerable care to get reliable and accurate results. The writer's method is briefly as follows:

Reagents (1) Pure KOH, fused, 100 grms. in 1 liter of previously boiled distilled water; boiled again 10 minutes.

(2) Pure K_2CO_3, fused, a nearly saturated solution in distilled water, previously freed from NH_3 and CO_2 by boiling.

Operation of Test.—Into each, of two clean 100 c. c. graduated flasks, 3 c. c. of the K_2CO_3 and 2 c. c. of the KOH solution are poured, and then 100 c. c. of the water to be examined

* Laboratory **1**, 442; J. prakt. Chem. **103**, 59.

† Dr. Smart makes use of this characteristic reaction in a skillful manner, but it is hardly original with him as Mallet intimates. Mallet's rep. loc. cit. p. 258.

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added; the flasks are stoppered and set away in a cool place for an hour.

Two filters are then washed with ammonia free hot water (containing some KOH) until the filtrate gives no reaction with Nessler's reagent.

From each flask about 30 c. c. are filtered before a portion is taken for nesslerizing; 40 c. c. more are filtered and then another 10 c. c. portion which is nesslerized; the first and last portions should of course agree.

The following figures illustrate the data which this method will afford. The above derived ammonia is described as "direct;" the figures represent parts per million:

	Direct.	*Distillation.*	*Diff.*
Diluted fresh sewage	9.62	–12.45	–2.83
Same sewage after standing 48 hours . .	16.80	–18.20	–1.40
A well water from a suspected district . .	0.016	–0.023	–0.007
Another well from same neighborhood .	0.005	–0.035	–0.030

The second result on the sewage indicates progress of decomposition of nitrogenous matter, the inorganic ammonia being increased and the organic ammonia consequently decreasing.

A contemplated series of examinations of a large number of waters whose general character is already well known will probably prove or disprove the value of this distinction abandoned by Wanklyn.

D. Among the many chances of error in the ordinary operation of the ammonia process, I am under the impression that the diminishing effect of the presence of even small quantities of CO_2, on the action of the Nessler reagent, is not fully appreciated. The danger is best avoided by adding a sufficiently large quantity of Nessler reagent; the addition of KOH to the standard ammonium chloride suggested by Rich * does not seem advisable. In the first distillate from a highly carbonated water it is well to add a second portion of Nessler to see if more color will be developed.

* Chem. News 28, 121.

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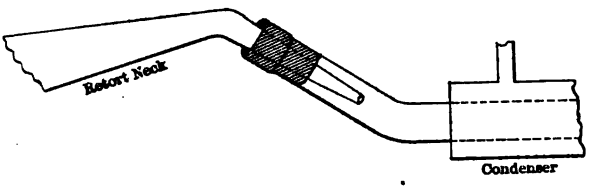
E. After many careful trials of different modes of connecting retort and condenser, some of which are utterly worthless (notably Wanklyn's *) the following device was adopted and has given perfect satisfaction. It is both convenient and reliable in every way. It consists in giving 3 in. of the upper end of the condenser an upward bend of 30°, and the drawn out end of the retort neck a downward bend of 45° (see fig.)



The end of the retort carries a cork which fits tightly in the condenser tube. The retort inclines slightly backward and no retention of distillate can occur at the connection. The passage from the retort to the condenser is visible.

The double angle makes manipulation of the connection exceedingly easy; in fact those who desire to retain the rubber tube connection will undoubtedly find this angle a positive convenience.

In closing this paper I realize that the sanitary problem discussed has been approached only on one side, that of the diagnosis; the sanitarian has also for consideration the purification of polluted water, a work in some respects even more emphatically necessary than detection of impurity; the chemist has much to do here also, for there is little prospect that the biologist can practicably solve the problems alone.

* See Mallet's rept. loc. cit., p. 279.

ANALYTICAL LABORATORY CORNELL UNIVERSITY.

REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its sixth annual report.

* Presented at the Buffalo meeting of the A. A. A. S. and reprinted at the request of the Chairman of the Committee.

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By the liberality of the Association the Committee secured 500 copies of the report for 1887, and these were distributed through the Secretaries of the American Chemical Society, the London Chemical Society, and the Washington Chemical Society, and directly by the Chairman of the Committee.

The Provisional List of Abbreviations of Titles of Chemical Journals, which formed Appendix B to the Report, was received by chemists with general approbation, and was reprinted in the Proceedings of the American Association for the Advancement of Science, Chemical News (London), American Chemical Journal (Baltimore), Journal of Analytical Chemistry (Easton), Journal of the American Chemical Society (New York), and was favorably noticed in the American Journal of Science (New Haven); this practically ensures its adoption.

During the year just closed, the Index to the Literature of the Spectroscope by Dr. Alfred Tuckerman has been printed by the Smithsonian Institution. This forms a work of about 400 pages, and contains 3,829 titles by 799 authors.

The Table of Specific Gravities for Solids and Liquids by Prof. F. W. Clarke is now in the compositor's hands and will soon be published by the Smithsonian Institution. This work is really a new and completely revised edition of Part I of the original "Constants of Nature."

An Index to the Literature of Columbium by Prof. Frank W. Traphagen has been completed and accepted by the Committee. Its publication has been undertaken by the Smithsonian Institution.

Dr. H. C. Bolton has compiled a Bibliography of Chemistry for 1887, the publication of which has been begun by the Smithsonian Institution.

Several chemists project indexes and have made more or less progress on them. Mr. Arthur A. Noyes is engaged on an index to the Literature of Ethylene; Prof. William P. Mason volunteers to index Methane; Mr. William Rupp undertakes to index Cæsium and Rubidium; Professor Traphagen plans to index Tantalum; Dr. H. C. Bolton has in preparation a Bibliography of the History of Chemistry, including Biography

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and Bibliography; and Dr. Alfred Tuckerman is engaged in indexing the Literature to Thermodynamics.

Several Bibliographies merit brief mention; Dr. Jesse P. Battershall's Food Adulteration and its Detection (New York, 1887), contains an Appendix with the title: "Bibliography, including Periodicals, Reports and General Works chronologically arranged." This includes about 275 titles. The Second Annual Report of the New York State Dairy Commismissioner (1886) contains a Bibliography of Milk by Mr. Edward W. Martin (pp. 156–170), and a Bibliography of Butter, Adulterations, Testing, etc., by Prof. Elwyn Waller, assisted by E. W. Martin and others (pp. 283–290).

Professor William H. Seaman calls the attention of the Committee to several lists of United States Patents which relate more or less to applied chemistry. These lists on subjects indicated by their titles are found in the following works: Charles Thomas Davis, Manufacture of Leather; the same, Practical Treatise on the Manufacture of Bricks, Tiles and Terra Cotta; the same, Treatise on Steam Boiler Incrustations; the same, Practical Treatise on the Manufacture of Paper; William T. Brannt, Treatise on Animal and Vegetable Fats and Oils. These are all published in Philadelphia, 1884–1887.

B. Tollens' Handbuch der Kohlenhydrate, Breslau, 1888, contains about 1500 references to the literature of carbohydrates.

Dr. Albert Brown Lyons publishes in the Pharmaceutical Era, under the title "Index Pharmaceuticus," a monthly list of books on pharmacy, chemistry and materia medica, as well as a list of original papers on these topics published in journals.

At the meeting of the British Association for the Advancement of Science held in 1886, a Committee was appointed for the purpose of reporting on the Bibliography of Solution. This Committee consists of Professors Tilden, McLeod, Pickering, Ramsay, Young, A. L. Leeds and Nicol (secretary), and presented its first report in 1887. This report sets forth the classification adopted, the list of journals (thirty-four in num-

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ber) desirable to index, and a summary of work accomplished. From this summary it appears that 355 titles have been catalogued from 588 volumes of eleven different periodicals. The Committee of the B. A. recommends as members of the Committee other gentlemen who have access to the journals on the list and who would be willing to take an active share in the work.

The Committee of the American Association expresses its gratification that the work begun by them in 1882 is now being supplemented by chemists in Great Britain.

Persons desiring copies of reports, indexes and other information should address the chairman, care of the Smithsonian Institution, Washington.

H. CARRINGTON BOLTON, *Chairman*
F. W. CLARKE,
ALBERT R. LEEDS,
ALEXIS A. JULIEN,
JOHN W. LANGLEY,
SAMUEL H. SCUDDER,
CHAS. K. WEAD.

NOTE ON THE MANUFACTURE OF CUPELS.

BY FRANCIS A. BLAKE.

Since the article in the July Journal was printed I am informed by Mr. S. Braden, assayer in charge of the U. S. Assay office at Helena, Montana, that a similar press has been in use there for over two years. I regret that I had not heard of this press in order to properly notice it. Mr. Braden uses the ordinary moulds, having two motions to the press—one to strike the cupel and the other to push out the cupel after moving the bed-plate.

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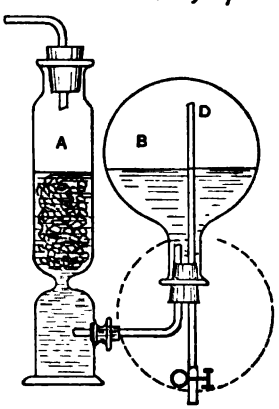
ABSTRACTS.

APPARATUS AND REAGENTS.

Starch Solution which will Keep.—G. Gastine, Bull. soc. chim. **50**, 172. 5 gms. potato starch and 1 centigramme of mercuric iodide are mixed with water to a thin paste and poured into about a liter of boiling water. The mixture is allowed to settle and the clear portion decanted for use. This solution keeps perfectly, and the amount of mercury present is so small that it has no bad influence even in presence of sulphides or sulphuretted hydrogen.

Sulphuretted Hydrogen Apparatus.—P. Chantemille, Bull. soc. chim. **50**, 170. A contains fragments of ferrous sulphide, held in position by a piece of perforated sheet lead. The flask is so large that when it is turned into the position shown by the dotted lines the end of D does not dip into the acid. If the tube through which the H_2S escapes is provided with a rubber tube and pinch cock the flask may be allowed to remain inverted ; the current of gas is then stopped by closing the pinch-cock and the gas collecting forces the acid over into B. Dilute hydrochloric is the acid used. The pinch cock on D may be dispensed with but is useful in preventing the escape of sulphuretted hydrogen into the air of the laboratory while the evolution of gas is going on. This apparatus may also be used for the preparation of other gases, such as hydrogen and carbon dioxide.



Improved Rubber Valve.— G. H. Bostock, Chem. News, **57**, 213. A bulb is blown upon a glass tube and covered with rubber tubing. This bulb is placed in the neck of the flask and acts as a valve.

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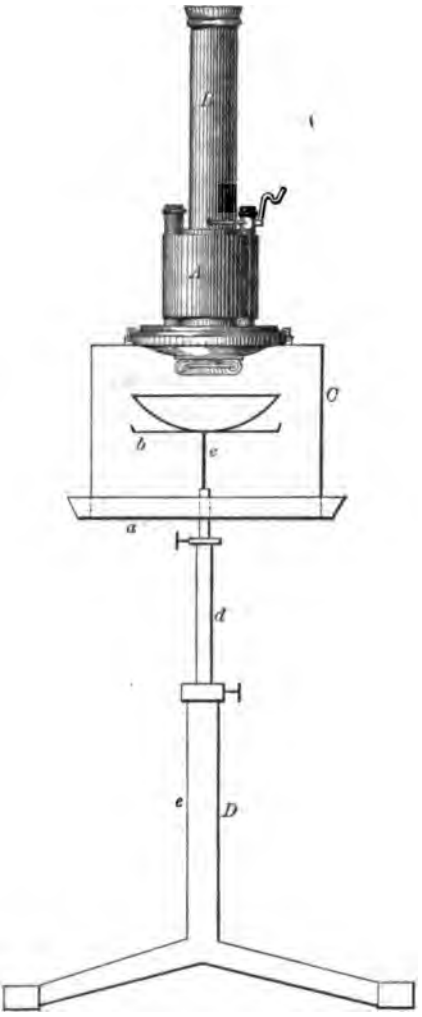

Use of Siemens' Regenerative Burner in Evaporation.—W. Hempel, Ber. **21**, 900. The regenerative burner A with draught chimney B rests upon the glass cylinder C. The lower end of this cylinder is placed upon the support *a* which is covered with sand; this makes a joint nearly gas tight. The dish resting upon *c* can be moved up and down by the screw from the outside; and *d* which supports the entire apparatus has a separate screw and moves independently. This allows the evaporating dish to be moved to and from the flame without opening the apparatus. Evaporation with this apparatus is very rapid. The author finds that the amount of sulphuric acid taken up from the flame depends upon the distance between the flame and the evaporating liquid. The nearer the flame to the surface of the liquid the less sulphuric acid taken up; and when in contact with it no absorption of sulphuric acid takes place. The heat is so great that sal ammoniac can readily be sublimed. The iron parts of the burner are not acted upon by the acid fumes so long as the burner is kept hot. Although this burner uses a large amount of gas, the gas used is small in proportion to the liquid evaporated.

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The Photo-chemical Estimation of Graded Tint.—E. J. Mills and J. Buchanan, J. Soc. Chem. Ind. **7**, 309. "The artifice consists essentially in photographing on an isochromatic plate and at one operation equal sized pieces of tissue exhibiting different degrees of the same tint. A negative is thus obtained from which any number of prints can be produced on 'gelatino bromide' paper, and each impression represents definitely in terms of silver the original grade of tint. All that is necessary is to make a sufficient number of impressions to enable the silver to be determined either volumetrically or gravimetrically.

"In our experiments pieces of cashmere of known weight were dyed in 'vats' of known strength and constant temperature, the proportions of coloring matter or mordant being varied. These pieces were mounted side by side on cardboard, and over all of them was mounted a second cardboard pierced all round with apertures of equal diameter. From the photographic negative a large number of prints were taken on Eastman Bromide Paper A. These prints were each exposed for the same length of time and were as far as possible developed under the same conditions. The exposure was so timed as to produce a slight effect only, where a slight tinctorial effect had to be represented. They were allowed to remain a much longer time than usual in the fixing bath, to make certain of the complete removal of the silver salts, and were then washed all night in running water. After drying, all the discs of one tint were cut out, incinerated in a porcelain crucible, and the ash treated with nitric acid free from chlorine. The nitric solution was evaporated completely to dryness, the residue dissolved in distilled water and again evaporated to dryness. The silver salt was then redissolved in distilled water, washed into a small flask, and made up to about 20 c. c. with water. A few drops of a solution of neutral potassium chromate free from chlorine were then added and the solution was titrated with centinormal sodium chloride."

NOTE.—Might not this method be used for comparison of colored solutions where the eye cannot detect slight differences, as, for example, in strong ammoniacal copper solutions. E. H.

Combustion Apparatus.—A. W. Stokes, Chem. News, **57**,

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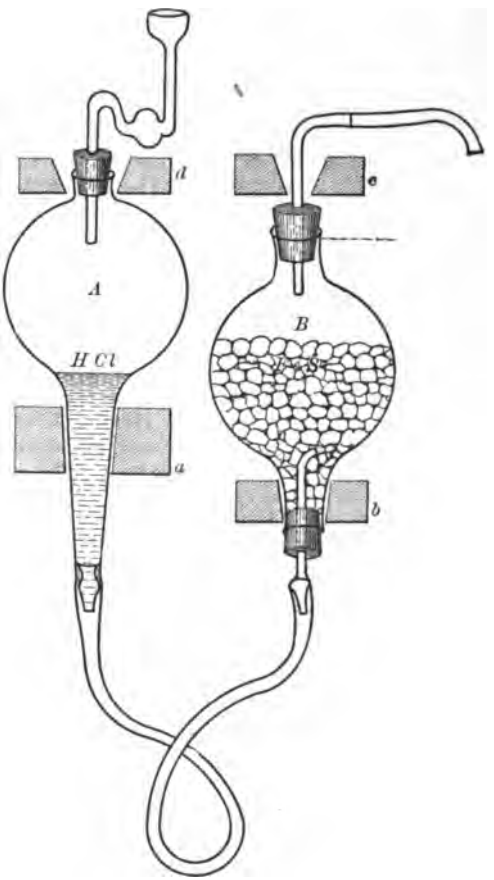
150. Instead of the fire-clay tiles used in the ordinary furnace pieces of asbestos card cut from sheet may be used. These pieces are lighter than tiles, are better non-conductors, cool rapidly and are not easily broken. When iron combustion tubes are used the corks may be dispensed with by polishing the ends and screwing over them caps polished inside. Between the polished surfaces a leaden washer is inserted and the cap screwed on firmly to make the joint gas tight. The temperature of the end of the tube must be kept below the melting point of lead.



Sulphuretted Hydrogen Apparatus.—J. H. J. Dagger, Chem. News, **58**, 127. *B* contains ferrous sulphide and communicates with *A* by means of the flexible rubber tube. The vessels are held by wooden forks which may be fastened permanently inside the hood or supported upon stands so as to raise and lower. The hydrochloric acid in *A* should be dilute, and by raising or lowering this the flow of gas is controlled. A cheap form of the apparatus may be readily constructed of two common lamp chimneys.

Modified Absorption Tubes.—J. T. White, Chem. News, **58**, 166. Test tubes closed at the top through which and

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reaching to the bottom passes an inlet tube; the outlet tube is melted into the top also, at one side. [It is difficult to see wherein lies the advantage, and the author admits that he has never tried them. A great objection to such tubes is that they must be hung to the arm of the balance when weighed. One great advantage of the Geissler potash bulb is, that it will stand upon the pan without support.—ED.]

For Separating Fusions from the Platinum Crucible.—L. L. de Koninck, Ztschr. angew, Chem. 1888, 569. After the mass is in quiet fusion one end of a platinum wire is placed in the fused material. This end of the wire is bent into a spiral, the other end terminates in a loop. The crucible is allowed to cool and then rapidly heated. As soon as melting begins next to the crucible, the solid cake is lifted out by a bent glass rod thrust through the loop. This device is especially useful in making fusion of titaniferous iron ore as the fused mass dissolves more rapidly.

NOTE BY THE EDITOR.—There is nothing new in this device, as I have used it myself for many years. At the Harrisburg meeting of the American Institute of Mining Engineers in October, 1881, Mr. Julian Kennedy described a method for hastening the solution of the bisulphate melt, of which Prof. de Koninck seems not to have heard. It consisted in adding strong sulphuric acid in considerable excess after the fusion, warming again and dissolving the mixture in warm water. In presence of the large excess of sulphuric acid titanic acid does not precipitate if too much water is not used. The excess of sulphuric acid is then neutralized with sodium carbonate. E. H.

Absorption of Carbon Monoxide by Cuprous Chloride.—This subject* has been further studied and discussed by Hempel (Ber. **21**, 898) and Drehschmidt (Ib. 2158) to whose papers we must refer the reader.

Sulphur Dioxide Apparatus.—E. R. Hodges, Chem. News, **58**, 187. Sulphur is burned under a funnel and the sulphur dioxide drawn through a Woulff's bottle containing water which absorbs it.

Improved Wash Bottle.—G. W. Slatter, Chem. News, **58**, 171. The mouth-tube is turned downwards and is connected with a short piece of rubber tubing which lies against the

* See this Journal **2**, 79.

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neck of the flask. The other end of this piece of tubing connected with a U-shaped tube, one leg of which is longer than the other and forms the mouthpiece. By blowing air into the flask and pressing the rubber tube against the neck of the flask with the thumb the water will be forced from the flask after the mouth has been withdrawn.

INORGANIC ANALYSIS.

The Determination of Arsenic.—R. C. Canby (a paper read before the Amer. Inst. of Mining Eng. at Birmingham, May, 1888.) "Take ½ to 1 gramme finely pulverized ore, and mix in a porcelain crucible with eight to ten times its weight of a mixture of equal parts of carbonate of soda and nitrate of potassium (Kerl. *Metallurgische Probirkunst* gives 4 to 5 nitre to 1½ soda). Gradually bring to fusion and keep so, three to five minutes. Cool. Disintegrate in hot water. Filter and wash with hot water. Acidify the filtrate with nitric acid, and boil to expel carbonic acid and nitrous fumes. Cool. Add an excess of an emulsion of oxide of zinc. The bottom of the beaker should have quite a layer of oxide of zinc, after stirring.

Should an unusually heavy precipitate of gelatinous silica or alumina be formed upon adding the oxide of zinc, it is well to filter before precipitating the arsenite of silver; in which case add additional oxide of zinc to the filtrate before adding the nitrate of silver, especially if the percentage of arsenic is liable to be great.

Add nitrate of silver in slight excess and stir vigorously. Filter and wash with cold water until the filtrate (wash-water) shows no silver. Dissolve on the filter the arsenite of silver together with the oxide of zinc in hot dilute nitric acid, allowing the filtrate to pass into a beaker free from chlorine. Cool. Add 1 c. c. ferric sulphate. Titrate with a standardized solution of ammonium sulphocyanide to a pale amber yellow, the same shade of color obtained in standardizing. 108 Ag = 25 As."

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Determination of Fluorine in Phosphates, Etc.—H. Lasne Bull, soc. chim., **50**, 167. The substance mixed with sand is placed in a dry flask and sulphuric acid added. The silicon tetrafluoride given off on heating is carried by a current of dry air through two absorbing bottles containing dilute caustic soda solution where it is absorbed. The caustic soda solution is then heated to boiling for fifteen minutes, allowed to cool, a few drops of phenolphtalein added and carbon dioxide passed through until the solution is decolorized. The solution is then heated to 50° and kept at this temperature for half an hour with an addition of ammonium carbonate from time to time. This throws down almost all the silica. The solution is then diluted to 125 c. c., filtered through a dry filter and 100 c. c. taken for analysis. In this way the tedious washing of the gelatinous silica is avoided. The error caused by neglecting the volume of the separated silica is too small to amount to anything. Usually the silica is completely separated, but to avoid all chance of error it is well to add a small quantity of oxide of zinc in ammoniacal solution to the 100 c. c. filtrate and to boil until the ammonia is driven off. During this operation it is best to pass a current of air through the liquid to prevent percussive boiling. The solution is filtered. A few drops of tropaeoline OO solution added and then dilute hydrochloric acid to neutralization; this point must, however, not be overstepped, otherwise the beaker will be rapidly attacked. A solution of sodium carbonate containing 0.5 gms. of the anhydrous salt is then added immediately, the solution heated to boiling to drive off excess of carbon dioxide and then a slight excess of calcium chloride added. The precipitate is filtered, washed, dried, ignited, evaporated to dryness with acetic acid in excess, the residue washed with water, dried, ignited and weighed.

The apparatus for decomposing the fluoride consists of a flask into which 3 tubes pass; one of these, open at both ends, dips below the surface of the sulphuric acid, and through this dry air passes into the flask. The second tube carries the gas given off into the absorbing flask, and a third tube is closed at

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the lower end, which dips into the acid, and is intended to hold a thermometer. The end of the tube dipping into the first absorption flask is enlarged so as to avoid danger of stoppage by the separated silica. This absorbing flask contains 2.5 gms. caustic soda in 25 c. c. water. The second absorbing flask contains 0.5 gms. caustic soda in the same amount of water. A slow current of air is drawn through the flask which is heated to 180 to 200° for an hour, the contents of the flask being shaken from time to time. When the operation is at an end the tubes of the absorption bottles should be washed into the solution and the united liquids, which must still be alkaline, treated as above directed.

The amount of substance taken should be sufficient to give 0.2 gm. calcium fluoride.

Reaction for Bismuth.—E. Leger. Bull, soc. chim. **50,** 91. The reagent employed is a solution of cinchonine nitrate in potassium iodide. 1 gm. cinchonine is converted into nitrate and to the warm solution a solution of 2 gms. potassium iodide in 100 c. c. water is added. When this solution is added to a solution of bismuth nitrate a yellowish orange precipitate forms. 1 part of bismuth can by this means be detected in 500000 of water. The conditions necessary for delicacy in this test are: avoidance of a large excess of nitric acid, employment of the reagent in excess, and entire absence of hydrochloric and sulphuric acids. Salts of silver, mercury, copper, cadmium and lead give precipitates with the reagent, some of which have some resemblance to that obtained with bismuth.

Titration of Hydroxylamine by Iodine. —Tamemasa Haga. J. Chem. Soc. **53,** 794. "The experiments here recorded show that high dilution with water causes hydroxylamine to give a higher titer with iodine than that calculated; that this effect of dilution is increased when sodium salts are present in large amounts; and that it is still more increased when carbonic acid is also present. They also show that with very high strength of the solution the titer may be too low."

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Volumetric Determination of Bromine.—J. T. White, Chem. News, **57**, 233, 245. Bromine is evolved on heating a bromide with potassium permanganate and aluminum sulphate; chlorides and iodides do not give off chlorine or iodine [this is untrue so far as iodine is concerned] 10 c. c. permanganate (1 to 25) is sufficient for 0.1 gm. Br.; the bromine is received in potassium iodide and the separated iodine determined with thiosulphate. [The author has not tested this process carefully and it certainly has no value in presence of iodine.—ED.]

Estimation of Nitrites.—T. C. Day, J. Chem. Soc. **53**, 422. The apparatus consists of a flask with inlet tube for CO_2 and an outlet with turned up end for passing the gas given off into a tube over mercury. The nitrite in solution is poured into the flask and an excess of solid ammonium chloride added until the solution is saturated, the flask is then filled with pure carbon dioxide, boiled and the nitrogen given off collected over mercury in a tube containing some caustic potash solution for absorbing the carbon dioxide, and the nitrogen measured. The reaction is

$$KNO_2+NH_4Cl=KCl+2H_2O+N_2.$$

According to this half the amount of the nitrogen obtained is that contained in the nitrite. Results obtained by the author on silver nitrite show that the method gives accurate results and that presence of nitrates has no influence.

Volumetric Estimation of Sulphuric and Phosphoric Acids.—J. T. White Chem. News, **57**, 165. Alkaline sulphates are treated with barium chloride, from the filtrate the excess of barium is precipitated with ammonium carbonate and the solution, after filtration, is evaporated to dryness, ignited gently and the chlorine estimated with silver nitrate and potassium chromate. If phosphoric acid is present it is separated with magnesia mixture, prepared with magnesium chloride, and the filtrate evaporated to dryness and ignited; the solution of the dissolved chlorides and sulphates is divided into two portions, in one of which the

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chlorine is determined directly while the other is treated as above directed. The difference gives the chlorine corresponding to the sulphate present.

Test analyses gave 0.0375 and 0.0741 instead of 0.0349 and 0.0769 gms. SO_3 taken.

Alkaline ortho-phosphates are precipitated by silver nitrate in excess in presence of calcium carbonate to neutralize free acid. The excess of silver nitrate is determined with a solution of ammonium chloride. Chlorides are separated by evaporating with excess of sulphuric acid and neutralizing with soda. The author obtained 0.0141 gms. P_2O_5 instead of 0.0152 gms. taken.

The Estimation of Phosphoric Acid with Silver Nitrate.—J. Clark. J. Soc. Chem. Ind. 7, 311: "The manure or mineral phosphate is dissolved either in nitric or sulphuric acid, the greater portion of the free acid neutralized with caustic soda, and to the cold solution acetate of soda containing free acetic acid is added in excess. If the addition of the acetate of soda produces a precipitate this must be filtered off, re-dissolved and re-precipitated with acetate of soda as before. The filtrate and washings are added to the previous filtrate, then excess of nitrate of silver, which will give an immediate precipitate of phosphate of silver, Ag_3PO_4, which is easily recognized by its yellow color, and the free acetic acid is neutralized with caustic soda till there is only a faint acid reaction to litmus paper. The slightest excess of caustic soda will cause a brown precipitate of oxide of silver if there is not too much ammoniacal salt present; but this oxide of silver dissolves easily on the addition of a few drops of dilute acetic acid. The precipitate of phosphate of silver, which will contain any chloride which may have been present, is thrown on a filter, thoroughly washed with water, then dissolved off the filter with hot dilute nitric acid, mixed with a little ferric sulphate, and the silver titrated with sulphocyanide as described by Volhard, and calculated to phosphoric acid.

The precipitate of phosphate of iron and alumina is dried, ignited, and weighed, then dissolved in acid, the iron

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determined volumetrically, calculated to phosphate of iron, and the balance assumed to be phosphate of alumina; or the oxide of iron may be separated with caustic soda and the alumina in the filtrate weighed as phosphate of alumina, using the precautions recommended by Robert T. Thomson (J. Soc. Chem. Ind. No. 3, Vol. 5).

The author found by this process in Bone Charcoal 30.16 and 30.15 per cent. phosphoric acid, by molybdate process 30.11 per cent.; in fish guano by silver process 10.45 and 10.55, by molybdate process 10.58; in superphosphate (soluble phosphoric acid) by silver process 13.48, by molybdate process 13.52 per cent.; in rock phosphate containing 4.07 per cent. alumina and 1.62 per cent. oxide of iron.

	a	*b*
By silver process	24.68	24.52
" " " calculated from phosphate of iron and alumina precipitate	6.85	6.99
Total	31.53	31.51
By molybdate process		31.43

"When the proportions of iron and alumina in a phosphate is very small (say about one-half per cent.), it is not necessary to add acetate of soda because they do not, in this proportion, materially affect the result, as about three-fourths of the phosphoric acid which would be precipitated as phospate of iron and alumina, is converted into phosphate of silver. Experiments made with native phosphate of alumina, containing neither lime nor magnesia, fully bears this out. In such cases excess of nitrate of silver may be at once added to the solution of the phosphate in sulphuric acid, and caustic soda added till the precipitate of phosphate of silver becomes brown, then acetic acid till the reaction is acid, and the precipitate is filtered off, dissolved in nitric acid, and titrated as already described."

Estimation of Sulphur in Burnt Pyrites.—J. Watson, J. Soc. Chem. Ind. **7**, 305. The total sulphur is determined

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by roasting 5.16 gms. ore and 2 gms. sodium bicarbonate in a platinum crucible over a Bunsen burner for 20 minutes, gently at first afterwards more strongly, the mass dissolved in boiling water filtered and the filtrate titrated with hydrochloric acid with methyl orange as indicator.

The soluble sulphur is found by boiling the same amount with sodium carbonate and determining the excess of sodium carbonate, after filtration, by titration with hydrochloric acid as above. In the discussion which followed the reading of the paper Mr. Martyn said that he "had used the method and found it to give good results as a rule, but under certain conditions the results were much too low."

The Volumetric Estimation of Sulphates.—D. Sidersky, Mon. Scien., Sep., 1888. This method depends upon the principle that if a solution of barium chloride be added to a solution of sodium carbonate, colored by phenol phtholeine, the barium carbonate at first precipitated, in presence of the excess of alkali, will take on a beautiful rose tint, which disappears suddenly as soon as the last trace of sodium carbonate has been decomposed by the barium chloride. By adding the barium solution drop by drop towards the end, the exact point of neutralization can be easily determined by the sudden disappearance of the red tint. This reaction is very sensitive, as there is no disengagement of carbonic acid to exercise an influence on the phenol phtholeine. The reaction is also effected by adding a solution of sodium carbonate to a solution of barium chloride to which phenol phtholeine has been added, but it is much less delicate, and hence in determinations it is better to operate it in the first manner. This reaction may serve for the volumetric determination of the alkaline carbonates, but as it cannot be used for that purpose in the presence of sulphates its utility would be limited. For the determination of sulphates it is made use of in the following manner:

Having given a neutral solution of an alkaline sulphate, for example, sodium sulphate, a known quantity of barium

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chloride in excess is added, and the liquid stirred and heated to boiling. The decomposition of the sulphate is almost immediate. There is next added an amount of sodium carbonate solution exactly equivalent to the amount of barium chloride used, together with some phenolphthaleine. If no sulphate were present the solution would be neutral, the two salts exactly decomposing each other, having been added in equivalent quantities. The sulphate however, having precipitated part of the barium, there is an excess of sodium carbonate, as is shown by the red color of the solution. This excess is exactly equivalent to the amount of barium chloride decomposed by the sulphate, and is estimated by running into the liquid from a burette a standard solution of barium chloride until the disappearance of the rose tint. If a normal solution has been used the volume run from the burette will be equivalent to the sulphate precipitated.

All the operations are conducted in one vessel, without filtering, which renders the process very easy and exact. It requires, however, that the solution of the sulphate to be determined contain no free acid or salts which are precipitated by barium chloride or sodium carbonate. The author gives details of processes for removing these, and thus applies his method to the determination of sulphates in many different mixtures. The sulphates of lime and magnesia are estimated by decomposing them with boiling sodium or ammonium carbonate and determining the alkaline sulphate produced. The method can thus be used to great advantage in water analysis. I. A. P.

Some Microscopical Chemical Reactions. — A. Streng, Chem. Zeit. Rep., **12**, 268. Test for tin : When a few drops of hydrochloric acid and platinic chloride are added to stannous chloride the platinic chloride is reduced giving to the solution an intense reddish brown color. This color is also obtained when a drop of platinic chloride is put into a solution containing a considerable quantity of hydrochloric acid and some stannous chloride, but if a small quantity of acid is present a brown flocculent precipitate is thrown down, which

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is compared under the microscope with the characteristic rhombohedral forms of potassium stannous chloride ($2KCl + SnCl_2$) or the more insoluble regular potassium stannic chloride (K_2SnCl_6). On account of its insolubility the test with stannic chloride is sharper than with stannous chloride but care must be taken not to mistake potassium chloride crystals for the stannic salt. Instead of the double salt with potassium the isomorphous caesium chloride may be used. This same reaction can be reversed for the detection of potassium and caesium. Rubidium can also be detected because its double salt with tin crystalizes in the monoclinic system. Instead of using a solution of uranium acetate for the detection of sodium the author uses the pulverized chemically pure salt to which a few drops of acetic acid have been added and puts it into the solution to be tested. The objection to a solution of uranium acetate is that it dissolves sodium from the glass.

For the detection of silicon, this element, if present, is combined as sodium fluosilicate which appears in the characteristic hexagonal form. Care must be taken to have the hydroflouric acid free from hydro-fluo-silicic acid which is never the case with the commercial product. S. C.

Testing Copper Sulphate for Iron.—E. Utescher, Chem. Zeit. Rep. **12**, 238. 0.5 gm. of copper sulphate is heated with 10 c. c. potassium thiocyanate solution (1–20) until the copper sulphate is dissolved and the black precipitate which is formed has become whitish, which shows that the copper thiocyanate is reduced. The precipitate is allowed to settle, and if the salt is free from iron the supernatant liquid is a pale yellow color; if it contains 0.04 per cent. ferrous sulphate the color is distinctly red, and if a higher per cent. of ferrous sulphate, a blood red. S. C.

Method for the Examination of Cerite.—J. Formánek, Chem. Zeit. Rep. **12**, 127. The author bases his method on the difficult solubility of the ceric hydrates and the easy solubility of the hydrates of Lanthanum and Didymium. The finely ground cerite is decomposed by concentrated sulphuric

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acid in a dilute hydrochloric acid solution and this solution is evaporated to dryness. The residue, while yet warm, is ground up and after cooling is added gradually to cold water which dissolves the sulphates of the above metals as well as the yttrium salt. The solution is then boiled and the sulphates of cerium lanthanum and didymium separate out. These are filtered off and washed with hot water.

The washings and the mother liquor are acidified with hydrochloric acid and the yttrium is precipitated with oxalic acid.

The sulphates of cerium, lanthanum and didymium are treated with a large excess of a concentrated solution of sodium hydroxide which precipitates cerium as cerous hydrate and this is converted into the ceric compound while yet in the solution by passing chlorine into the liquid until the entire mass is orange colored. The residue is then filtered off and thoroughly washed by decantation, after which it is treated with dilute hydrochloric acid (1–10) and allowed to stand for about an hour in the cold. The clear liquid which contains nearly all the lanthanum and didymium and only a trace of cerium, is poured off and the treatment with dilute hydrochloric acid is repeated until the cerium is free from lanthanum and didymium. The small quantity of cerium contained in the solution of the latter metals is precipitated by Prof. Stolba's method with oxide of zinc and potassium permanganate, and filtered off. The filtrate is strongly acidified with hydrochloric acid and boiled with a slight excess of oxalic acid which precipitates the lanthanum and didymium. The oxalates are washed with slightly acidified hot water, dried, and heated until converted into the oxides from which the metals may be separated by the usual methods.

It has been found that when the solution of these metals is strongly acid and the oxalate precipitate is filtered off immediately there is no danger of zinc and manganese being precipitated with them. S. C.

Estimation of Boric Acid by the Polariscope.—Landolt, Ber. **21**, 218. The addition of boric acid to a tartaric acid solution increases the rotatory power of the solution. 20 gms. of dry tartaric acid were dissolved in solutions of boric acid of

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varying strengths and the solutions made up to 100 c. c. and polarized at 20° in a Laurents' half-shadow polaristrobometer, the tube having a length of four decimeters. From the experiments it was found that if C be the number of gms. boric acid per liter, and x the angle of rotation observed after addition of the tartaric acid

$$C = 1.4 \times x - 14.4$$

The results obtained were as follows:

Observed $20\frac{a}{D}$ *for* $l = 4$ *dm.*	*C taken.*	*C found.*	*Difference.*
10°.20	0	——	——
11.65	2	1.9	—0.1
13.03	4	3.8	—0.2
14.57	6	6.	0.0
16.18	8	8.2	+0.2
19.10	12	12.3	+0.3
21.81	16	16.1	+0.1
24.29	20	19.6	—0.4

Analysis of a Mixture of Potassium and Sodium Chlorides with the Polariscope—F. Schutt. Ber. **21**, 2586. When sodium chloride is added to a solution of potassium tartrate the rotatory power of the solution is diminished, while the addition of potassium chloride increases it in a less degree. It was found that the conditions were best fulfilled when 22 gms. potassium tartrate were taken, dissolved in water, 20 gms. of the mixture to be tested added to this and the solution diluted to 100 c. c. and polarized at 20° in a 4 dm. tube. A fractional part of 22 gms. and 20 gms. can of course be used, but there must be sufficient solution to fill the tube. The potassium tartrate is dried at 110° C for several hours before weighing.

It was found that the rotatory power of such a solution was 62.06 when the addition consisted of sodium chloride entirely, and 73.72 when it was entirely of potassium chloride. This gives a difference of 11.66 scale divisions for 100 per cent. difference, or, as $\frac{1}{20}$ division can be read $\frac{1}{234}$ of 100 per cent. = 0.43 per cent. difference can be detected in this way. If x be the observed rotation above 62.06 in $\frac{1}{10}$ scale divisions (Schmitt & Haensch's Saccharimeter) and y the percentage

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amount of potassium chloride in the mixture to be examined then

$$y=3340.4-\sqrt{11158270-(5527.3x+x^2)}\,*$$

from which the following tables have been calculated.

Scale Divisions.	KCl p ct.	Scale Divisions.	KCl p ct.	Scale Divisions.	KCl p ct.	Scale Divisions.	KCl p ct.	Scale Divisions.	KCl p ct.	Scale Divisions.	KCl p ct.
62.06	0.00	64.00	16.13	66.00	33.00	68.00	50.04	70.00	67.30	72.00	84.79
10	0.33	10	16.97	10	33.84	10	50.89	10	68.17	10	85.67
20	1.16	20	17.81	20	34.69	20	51.75	20	69.04	20	86.55
30	1.99	30	18.65	30	35.54	30	52.61	30	69.91	30	87.43
40	2.81	40	19.49	40	36.39	40	53.47	40	70.78	40	88.32
50	3.64	50	20.33	50	37.24	50	54.33	50	71.65	50	89.20
60	4.47	60	21.18	60	38.09	60	55.19	60	72.52	60	90.08
70	5.30	70	22.02	70	38.94	70	56.06	70	73.39	70	90.96
80	6.13	80	22.86	80	39.79	80	56.92	80	74.27	80	91.85
90	6.96	90	23.70	90	40.64	90	57.78	90	75.14	90	92.73
63.00	7.79	65.00	24.54	67.00	41.49	69.00	58.65	71.00	76.02	73.00	93.61
10	8.62	10	25.39	10	42.34	10	59.51	10	76.90	10	94.50
20	9.45	20	26.23	20	43.20	20	60.38	20	77.77	20	95.38
30	10.29	30	27.07	30	44.05	30	61.24	30	78.65	30	96.27
40	11.12	40	27.92	40	44.90	40	62.10	40	79.53	40	97.16
50	11.95	50	28.76	50	45.76	50	62.97	50	80.40	50	98.04
60	12.79	60	29.60	60	46.61	60	63.83	60	81.28	60	98.93
70	13.62	70	30.45	70	47.47	70	64.70	70	82.16	70	99.82
80	14.46	80	31.30	80	48.32	80	65.56	80	83.03	72	100.00
90	15.29	90	32.15	90	49.18	90	66.43	90	83.91		
62—63.9		64—65.9		66.0—67.9		68.—0 69.9		70.0—71.9		72.0—73.7	

Rotation.	KCl p ct.	Rotation.	KCl p ct.	Rotation.	KCl p ct.	Rotation.	KCl p ct.	Rotation.	KCl p ct.	Rotation.	KCl p ct.
0.01	0.08	0.01	0.08	0.01	0.09	0.01	0.09	0.01	0.09	0.01	0.09
0.02	0.17	0.02	0.17	0.02	0.17	0.02	0.17	0.02	0.17	0.02	0.18
0.03	0.25	0.03	0.25	0.03	0.26	0.03	0.26	0.03	0.26	0.03	0.27
0.04	0.33	0.04	0.34	0.04	0.34	0.04	0.34	0.04	0.35	0.04	0.35
0.05	0.42	0.05	0.42	0.05	0.43	0.05	0.43	0.05	0.44	0.05	0.44
0.06	0.50	0.06	0.51	0.06	0.51	0.06	0.52	0.06	0.52	0.06	0.53
0.07	0.58	0.07	0.59	0.07	0.60	0.07	0.60	0.07	0.61	0.07	0.62
0.08	0.67	0.08	0.67	0.08	0.68	0.08	0.69	0.08	0.70	0.08	0.71
0.09	0.75	0.09	0.76	0.09	0.77	0.09	0.78	0.09	0.79	0.09	0.80

* See the original paper.

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In using this table readings to $\frac{1}{10}$ division are obtained from the upper table and to this the differences of less than $\frac{1}{10}$ obtained from the lower table are added; for example: Suppose the reading to be 66.76. The amount corresponding to 66.70 obtained from the upper table is 38.94 per cent. KCl. To this is to be added .06 from the third column of the lower table = 0.51 ; together 39.45 per cent. KCl.

The authors tested the method by polarizing mixtures of the two chlorides containing 5, 10, 15, 20, 25 . . . . . 95 per cent. KCl and obtained results which differed from the theoretical from nothing to 0.56 per cent ; in the greater number of cases the error was much smaller than this.

Since one division of the scale on this instrument is equal to almost exactly $\frac{1}{3}$ degree, $\frac{1}{20}$ division = 1 minute on those polariscopes having a circular graduation.

IRON AND STEEL.

EDITED BY P. W. SHIMER.

Determination of Sulphur in Coke.—L. Blum, Ztschr. anal. Chem., 1888, 455. It is well known that the wet methods for determining sulphur in coke often give much lower results than the fusion methods. According to the author there seemed to be considerable difference of opinion as to the cause of this. By heating 3 gms. finely powdered coke with a solution of potassium chlorate and strong hydrochloric acid; evaporating to dryness; re-solution and filtration from the unoxidized coal and precipitation by barium chloride he obtained, in ten samples of coke, results varying from 0.164 to 0.276 per cent. sulphur. These results, as will appear, were far too low.

By heating 3 gms. of coke with a saturated solution of bromine in concentrated hydrochloric acid, evaporation to dryness, re-solution, filtration and precipitation by barium chloride, the results agreed closely with those obtained by the above potassium chlorate method.

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By using aqua regia as the oxidizing agent the results were only slightly higher than those obtained by the two preceding methods.

The author now dried the coal-residue from the aqua regia treatment, and fused it with an oxidizing fusion mixture. In addition to the 0.295 per cent. sulphur yielded him by the aqua regia method, he found 0.798 per cent. sulphur in the residue from the aqua regia treatment.

By fusing 1 grm. of coke with a mixture of 16 parts sodium chloride, 8 parts potassium nitrate and 4 parts sodium carbonate; solution of the fused mass in water, acidifying with HCl, evaporation to dryness, re-solution in water, filtration and precipitation by barium chloride solution, he obtained from 0.907 to 1.147 per cent. sulphur in the same cokes which had yielded him only 0.164 to 0.276 per cent. by the wet method.

The author concludes that sulphur obtainable by the wet methods is that which exists in the coal as metallic sulphides, and that which is only obtainable by fusion is in organic combination.

[Thomas M. Drown published, in 1881, in the Trans. Am. Inst. Min. Eng. Vol. IX, p. 656, under the title, "The Condition of Sulphur in Coal and its Relation to Coking," the results of a complete investigation of this whole subject. P. W. S.]

Determination of Sulphur in Iron.—L. L. deKoninck, Ztschr. für angewandte Chemie, 1888, 311. The H_2S evolved by dissolving iron in hydrochloric or sulphuric acid is led through a solution containing 4 per cent. of cyanide of mercury and 2 per cent. of ammonium chloride. The sulphide of mercury formed is filtered off and treated with an excess of bromine-water. Bromide of mercury and sulphuric acid are formed, which latter is precipitated by barium chloride in the usual manner.

Determination of Carbon in Iron and Steel.—L. L. de Koninck, Ztschr. anal. Chem., 1888, 463. The carbon obtained by dissolving iron or steel in cupric-ammonium chloride solution is very apt to retain chlorides, unless washed

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with the utmost care. This chlorine is given off with the carbonic acid on treating the carbon residue by the wet method with strong sulphuric and chromic acids. This may be avoided by adding some silver sulphate to the solution in the oxidation flask. The silver chloride formed is said to be entirely unaffected by the mixture of strong sulphuric and chromic acids.

New Method for the Estimation of Sulphur in Steel and Steel-Making Iron.—J. O. Arnold and Henry J. Hardy, Chem. News, **58**, 71. The authors give the details of two methods for sulphur determination, one colorimetric and approximate, but rapid, the other volumetric and accurate. In both methods the sulphur is evolved as H_2S by heating the finely-divided metal with dilute sulphuric acid (1 in 7). In the volumetric method the H_2S is passed through a series of tubes each containing just enough of an acid solution of acetate of lead to fix as sulphide 0.01 per cent. of sulphur in 2 grms. of steel. At the end of the operation the number of cylinders precipitated indicates the number of hundreths of sulphur that the sample contains.

New Mixtures for Separating Carbon from Pig-Iron and Steel.—T. W. Hogg, Chem. News. **58**, 199. It is proposed to add ferric chloride solution to the solution of cupric chloride in order to readily dissolve the cuprous chloride formed on dissolving iron in it.

Influence of Sulphur upon Eggertz's Carbon Color-Test.—T. W. Hogg, Chem. News, **58**, 175. The author finds that sulphur separates as such when steel is dissolved in nitric acid. Solutions of steel containing more than a very small amount of sulphur are therefore more or less turbid, and this leads to over-estimation of the color-intensity.

ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

Oxygen.—Cooke and Richards (Am. Chem. Jour., **91**, 191) have published a note supplementary to their paper on this

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subject. It will be remembered that their method of determination consisted in weighing hydrogen in large glass globes, burning the gas, and then weighing the water so formed. But Rayleigh has since shown that the volume of a globe so used is not the same when it is full and empty. When empty the globe is sensibly compressed ; and hence the *tare* of the globe is altered. Cooke and Richards have investigated the amount of the correction to be applied in the case of the glass globes used by them, and find it to average 1.98 milligrammes in each weighing of hydrogen. This amount is to be added to the weights previously given, and its effect is to reduce the atomic weight of oxygen from 15.953 to 15.869.

Scott, (Nature, March 8, 1888) has continued his researches on the composition of water by volume, and finds the ratio of H to one volume of oxygen to be

1.9972
1.9968
1.9980
1.9962

Compare this Journal, vol. 2, p. 95.

Keiser, (Am. Chem. Journ., 10, 249) has published his final results on the atomic weight of oxygen, as determined from the combustion of hydrogen occluded by palladium. He gives full details as to methods of manipulation, shows that the hydrogen weighed was presumably pure, and that no other gas was occluded by the palladium. The combustions were effected over copper oxide. Ten experiments gave results as follows :

.34145	grammes	H	gave	3.06338 of H_2O.	O=15.943
.68394	"	"	"	6.14000	15.955
.65529	"	"	"	5.88200	15.952
.65295	"	"	"	5.86206	15.954
.66664	"	"	"	5.98116	15.944
.66647	"	"	"	5.88341	15.955
.57967	"	"	"	5.20433	15.958
.66254	"	"	"	5.94758	15.952
.87770	"	"	"	7.86775	15.950
.77215	"	"	"	6.93036	15.951
Sum 6.55880				58.86263	15.9482

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This agrees very nearly with the earlier value given by Cooke and Richards.

Zinc.—Morse and Burton, (Am. Chem. Journ. 10, 311) have redetermined the atomic weight of zinc by the oxidation of the metal. Pure distilled zinc was treated with nitric acid in a porcelain crucible, and the evaporated mass, after gentle heating, was strongly ignited in a muffle at a temperature sufficiently high for melting steel. The crucible itself was protected by a second crucible, which last was within a third, and in weighing the first and second were kept together, being tared against a similar set. This process, previously used by Erdmann, although with differences of detail, has been objected to by Marignac; who claims that zinc oxide dissociates at high temperatures, and also that it retains oxide of nitrogen.

These objections are shown by Morse and Burton to be groundless. Fifteen experiments gave results as follows, when O = 15.96.

Wt. of Zn.	*Wt. of ZnO.*	*At. Wt. Zn.*
1.11616	1.38972	65.119
1.03423	1.28782	65.091
1.11628	1.38987	65.119
1.05760	1.31681	65.118
1.04801	1.30492	65.105
1.02957	1.28193	65.113
1.09181	1.35944	65.110
1.16413	1.44955	65.095
1.07814	1.34248	65.095
1.12754	1.40400	65.093
.91112	1.13446	65.109
1.10011	1.36981	65.101
1.17038	1.45726	65.111
1.03418	1.28436	65.100
1.05505	1.31365	65.104
	Mean,	65.106

Osmium.—The atomic weight of this metal, hitherto practically undetermined, has been investigated by Seubert. (Be-

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richte, **21**, 1839). The salts Am_2OsCl_6 and K_2OsCl_6 were used for the determinations. In the first case the salt was heated in hydrogen, and the ammonium chloride given off was collected in a suitable apparatus. The residual osmium was weighed, and the ammonium chloride was precipitated by silver nitrate and the chlorine estimated as AgCl. Three experiments came out as follows :

	Salt.	*Os.*	*AgCl.*
	1.8403	.7996	3.5897
	2.0764	.9029	4.0460
	2.1501	.9344	4.1950
Sum.	6.0668 grm.	2.6369 grm.	11.8307 grm.

2.1345 grammes of another sample of salt gave .9275 of osmium and 4.1614 of AgCl.

From the sum of the three experiments we have the following values :

From ratio	Am_2OsCl_6 : Os	Os=190.83
" "	Am_2OsCl_6 : 6AgCl	Os=191.85
" "	Os : 6AgCl	Os=191.27

From the single experiment last cited the same ratios give respectively, Os=190.74, 191.96, and 191.27.

The salt K_2OsCl_6 was similarly treated with hydrogen, and the Cl_4 was weighed finally as AgCl. The residue 2KCl was also estimated. Two samples of salt gave results as follows :

	Salt.	*2KCl.*	*4AgCl.*	*Os.*
1st.	2.5148	.7796	2.9837	——
2nd.	2.1138	.6547	2.5076	.8405

From these data we have the following figures for the atomic weight desired.

	1st.	*2d.*
Ratio K_2OsCl_6 : 2KCl	Os=189.72	190.18
Ratio K_2OsCl_6 : 4AgCl	Os=191.94	192.00
Ratio K_2OsCl_6 : Os		Os=191.60
Ratio Os : 2KCl		Os=191.02
Ratio Os : 4AgCl		Os=191.76

The mean of all the values is Os=191.12, or, approximately, 191 ; which figure Seubert regards as still slightly too high.

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Meyer and Seubert's values for the atomic weights of Ag, K, N and Cl were used in the calculation with H=1. The determination, although still leaving much to be desired as regards sharpness, is interesting as proof that osmium does not behave exceptionally with respect to the periodic law.

Platinum.—Dittmar and McArthur (Trans. Roy. Soc. Edinburgh, **33**, 561) from experiments of a complex kind upon the chloroplatinates of potassium, ammonium, and rubidium, conclude that Seubert's value for Pt, 194.8, is too low, and that the figure 195.5 is more nearly true.

Seubert, (Berichte **21**, 2519) replies to the foregoing paper, and maintains his own determination. He calls attention also to Helberstadt's confirmation of his results, which Dittmar and McArthur seem to have overlooked.

ORGANIC ANALYSIS.

The Estimation of Saccharine Matters.—M. W. Bishop, Mon. Scien., June, 1888, p. 641. The author's lengthy paper is devoted to a discussion of methods for the determination of saccharose, glucose and dextrin, either alone, or in presence of each other. The author claims that saccharose can be successfully inverted for determination in presence of dextrin, and that dextrin can be saccharified in presence of saccharose, or more correctly, in presence of inverted sugar. Hydrochloric acid is found to be the best acid for this purpose. It is preferable to sulphuric acid, because it is less destructive to saccharine matters than the latter.

.5 c. c. of concentrated hydrochloric acid is found to be sufficient to invert completely in 10 minutes 8 grams of sugar dissolved in 50 c. c. of water at 95°. The action can be continued for 15 minutes without appreciable change. If the amount of acid be increased to 2 c. c. the inverted sugar begins to be attacked. Prolonged treatment has the same effect. Dextrin, when treated with .5 c. c. of hydrochloric acid under the same conditions, is not sensibly acted upon, and it is found that the maximum of saccharification is obtained by using 2

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to 4 c. c. of the acid and heating from 3 to 5 hours at 95–100°. More acid and longer treatment diminish the result in reducing sugar. Glucose is not acted upon by 15 minutes treatment with .5 c. c. of acid as above.

These facts being ascertained by a large number of experiments, the following methods of analysis are proposed:

The liquid to be examined is first decolorized, either by bone black or sub-acetate of lead, as deemed advisable, and then diluted, so that 10 c. c. will reduce about 10 c. c. of Fehling's solution. If the examination by the saccharimeter shows that sugar or glucose, or a mixture of the two may be present, the liquid is treated as follows:

50 c. c. are placed in a 100 c. c. flask with 1 c. c. of hydrochloric acid, sp. gr. 1.09; the flask is plunged into a bath of water at 60° and the temperature rapidly raised to 95°. At the end of 10 minutes the flask is cooled and the liquid diluted to 100 c. c. The solution being again examined by the saccharimeter the presence or absence of saccharose in the original liquid is ascertained. If present, the determination of the inverted sugar by Fehling's solution will give the amount. If the specimen contained no saccharose the result of the determination by the Fehling's solution will very nearly coincide with the result obtained in the original liquid.

To estimate the dextrin 50 c. c. of the decolorized liquid are placed in a 150 c. c. flask with 4 c. c. of hydrochloric acid, sp. gr. 1.09. The flask is closed by a cork supplied with a long tube to condense the vapors and maintain the concentration of the acid. The flask is placed on a water bath and heated to 95–100° for 3 hours. It is then cooled and the liquid diluted to 150 c. c. Examination by the saccharimeter will then show whether dextrin was originally present, and if so its amount is determined by estimating with Fehling's solution the reducing sugar produced, allowance being made, of course, for the reducing sugar found in the original liquid and that coming from the saccharose, if present. In this way, the saccharimeter being used to indicate the nature of the saccharine matter and Fehling's solution to determine the reducing

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sugar produced in the operations, the author has estimated the saccharine matters in a large variety of commercial products, the results of which are given in his paper. I. A. P.

Note upon Morphine.—Dr. O. Hesse, Pharm. Jour. and Trans., March 24, 1888. In this paper the author reaffirms his former statement that morphine hydrate loses its water of crystallization between 90° and 100°. Numerous experimental determinations have convinced him that the authorities are not correct in saying that it becomes anhydrous only at a temperature above 100°. Even at 60° the crystals become dull from the loss of water of crystallization, but become anhydrous only at 90°. At this temperature, however, considerable time is required for the complete expulsion of the water. At 100° the action is immediate. The author's experiments also show that the quantity of the water of crystallization is exactly one molecule per molecule of morphine.

Most works on chemistry say that the temperature of fusion of morphine is not constant, but is a little below 120°, at which temperature it decomposes. The author has found that the temperature of fusion, though not constant, is nearly 230°, and that it does not decompose until this temperature is reached.

As to the new reaction of morphine described by Lister Armitage,* the author is not inclined to accept the explanation of it offered by Mr. Armitage. A dilute solution of a salt of morphine being added to a dilute solution of ferric chloride and potassium ferricyanide an intense blue coloration is immediately produced in the liquid. According to Armitage this is produced by the reduction of the ferric chloride by the morphine salt and the consequent reaction with the potassium ferricyanide. The author of the present paper thinks, however, that it is due to the formation of pseudo-morphine and hydroferrocyanic acid, the reaction being, with hydrochloride of morphine and postassium ferricyanide, as follows :

$$8(C_{17}H_{19}NO_3, HCl) + 8K_3FeCy_6 = 4(C_{34}H_{38}N_2O_6, 2HCl) + 6K_4FeCy_6 + 2H_4FeCy_6.$$

After the mixture of the two solutions the liquid acquires

* Ann. Chem. 235, 1.

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an acid reaction and, if the solution is not too dilute, ferrocyanide of pseudo-morphine will be found deposited in the form of a resinous precipitate, tolerably soluble in water. The reaction, then, is due to the ferric chloride acting upon the potassium ferrocyanide produced. The reaction is shown in a striking manner as follows :

A small quantity of a moderately concentrated solution of a salt of morphine is added to a very dilute solution containing equivalent quantities of ferric chloride and potassium ferricyanide. A single drop suffices to produce in the iron solution a most intense blue coloration. If the morphine solution be extremely dilute, for example 1 part in 1000, no coloration is observed immediately, but in a few seconds the presence of morphine is shown by the appearance of blue streaks in the liquid. I. A. P.

Characteristic Reactions of the Artificial Coloring Matters.—Weingaertner and Zetter, Chem. Ind., March, 1888. The table of reactions given below has been compiled by G. Zetter and is the result of the extension and completion of the tables of Weingaertner. The coloring matters in every-day use are arranged in groups according to characteristics which are easily recognized; such as color, solubility or insolubility in water, and the basic or acid function of the radicals. The coloring matters in each group are recognized by specific reactions which are given.

I.—BASIC COLORS SOLUBLE IN WATER.

The addition of a small quantity of alkali produces a precipitate or decolorizes the moderately concentrated solution.

1. *Fuchsine, Neutral Red, Safranine.*

Concentrated sulphuric acid dissolves fuchsine to a brown solution, neutral red to bluish green and safranine to green.

2. *Phosphine, Flavaniline.*

Alkalies throw down from an aqueous solution of phosphine a yellow flocculent precipitate which dissolves in ether to a yellow solution with strong green fluorescence. In the same

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conditions flavanline gives a colorless precipitate which communicates to ether a blue fluorescence.

3. *Malachite green*, *brilliant green*, *methyl green.*

Ammonia produces a rose red or gray precipitate. Sulphuric acid changes the color to yellow, changing again to green on diluting with water : *malachite green.* Little or no precipitate with ammonia ; the liquid becomes yellow by the addition of sulphuric acid; regainiug its original color very slowly on diluting with water : *brilliant green.* Ammonia decomposes the solution without any precipitate ; the acid changes the color to a permanent yellow : *methyl green.*

4. *Methyl blue*, *neublau B and D*, *new blue*, *muscarine.*

Caustic soda gives a violet black precipitate, sulphuric acid colors the solution grass-green : *methylene blue.* Caustic soda gives a blue-black precipitate : *neublau B and D.* Solution violet when warm, green when cold, with caustic soda a brownish-red coloration : *new blue.* Caustic soda gives a brownish-red precipitate, tannin an indigo blue precipitate : *muscarine.*

5. *Methyl violet*, *neutral violet*, *mauveine*, *amethyst*, *crystallized violet.*

Sulphuric acid gives a yellowish brown coloration, changing to green and violet-blue by dilution : *methyl violet.* (*Hofmann violet*). Sulphuric acid gives a bright violet color, changing to blue by dilution : *neutral violet.* Sulphuric acid produces a gray color, changing to sky-blue and violet-red by dilution : *mauveine* (*rosolane*). Sulphuric acid gives a green color, becoming blue by dilution : *amethyst* (*fuchsine violet.*)

6. *Auromine*, *chrysoidine*, *vesuvine*, *victoria blue.*

Yellow color, the alkalies producing in the aqueous solution a milky white precipitate ; sulphuric acid decolorizes the solution slowly on warming : *auramine.* Orange color, dissolving to a brownish yellow solution in sulphuric acid : *chrysoidine.* Brown color, orange upon silk ; soluble to a pale liquid in sulphuric acid : *vesuvine.* Blue, changing to brown-red, then to bluish-green, by sulphuric acid : *victoria blue.*

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II. Acid Colors, Soluble in Water, Thrown Down from their Aqueous Solutions or not changing by the Addition of an Acid.

A small quantity of caustic alkali does not modify them.

1. *Phthaleines, corallines.*

Sulphuric acid dissolves the coloring matter to a yellow solution; by heating the dry vapors of hydrobromic acid are driven off; hydrochloric acid precipitates from the aqueous solution orange flakes of *eosine.* Sulphuric acid dissolves to gold yellow solution; some disengagement of hydrobromic acid on heating: hydrochloric acid precipitates from the aqueous solution brown flakes: *safrosine.* Same reactions with sulphuric acid and by heating; flesh colored precipitate with HCl: *phloxyne.* Sulphuric solution orange; vapors of iodine driven off on heating the dry color; no fluorescence in the aqueous solution: *bengal rose.* Solutions brownish yellow, decolorized, with the formation of a brown precipitate, by the addition of HCl: *mauveine, chrysoline.* Solutions brick red; yellow precipitate with HCl; no disengagement of vapors on heating the dry colors; *coralline, aurine.*

2. *Sulphoconjugated derivatives of the rosanilines, indulines, nigrosine.*

Acid fuchsine: Aqueous solution bluish-red, sulphuric solution yellow, changing to red on being diluted.

Helvetia green (acid green): Aqueous solution pale green, decolorized by the alkalies.

Alkaline blues B to 6 B: Decolorized by the alkalies.

China blue: Aqueous solution blue, not modified by the alkalies.

Acid violet: Aqueous solution violet, decolorized by ammonia. Sulphuric acid dissolves the color to an orange solution, changing to grayish violet by dilution.

Indulines, nigrosine: Aqueous solution grayish-violet from which HCl precipitates bluish flakes; violet-red precipitate with ammonia.

3. *Nitrophenols and aurantia.*

Picric acid: Aqueous solution greenish-yellow, turning to

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deep yellow when treated with alkalies: no precipitate with HCl; dry product mixed with sodium carbonate and heated detonates.

Yellow of Martius: Yellowish-white precipitate with HCl, insoluble in ether.

Aurantia: The concentrated aqueous solution is red, yellow when diluted; an excess of alkali produces a deep red precipitate.

4. *Azo derivatives of benzidine and erythrosine.*

Congo red: Aqueous solution orange, with HCl blue.

Benzopurpurin: Aqueous solution orange, with HCl brown precipitate.

Azoblue: Aqueous solution violet blue, turning to blood red with the alkalies.

Erythrosine: Aqueous solution bluish-red; by heating the dry coloring matter iodine is driven off.

5. *Other azo compounds.*

Solid yellows R and G: With sulphuric acid yellow.

Diphenylamine yellow (*Tropeoline 06*): With sulphuric acid violet.

Azoflavine: With sulphuric acid red.

Methyl aud ethyl orange: With sulphuric acid yellow.

Yellow N. Poirrier: With sulphuric acid bluish-green.

Luteoline: With sulphuric acid green-yellow.

Tropeoline: With sulphuric acid orange brown.

Mandarine: With sulphuric acid carmine red.

Scarlet of Biebrich: With sulphuric acid green.

Scarlet of croceine: With sulphuric acid indigo blue.

Xylidine scarlet: With sulphuric acid violet.

Scarlet of croceine 7 B: With sulphuric acid blue.

Scarlel R, 4 and G: With sulphuric acid eosin red.

Coccine: With sulphuric acid fuchsine.

Roccelline: With sulphuric acid violet.

Bordeaux G. aud R: With sulphuric acid blue.

6. *Derivatives of anthracene.*

Alizarin S.: Aqueous solution brownish-yellow, ammoniacal, fuchsine red.

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Ceruleine S.: Agueous solution olive-brown, ammoniacal-green.

Alizarin Blue S.: Agueous solution red-brown, ammoniacal, bluish-green.

III.—Colors Insoluble in Water.

1. *Gallocyanine, galleine, ceruleine, galloflavine.*

Gallocyanine: Caustic soda solution violet; sulphuric acid solution blue.

Galleine: Sulphuric acid solution indigo blue.

Ceruleine: Caustic alkali solution green; sulphuric acid solution green.

Galloflavine: Caustic alkali solution yellow; sulphuric acid solution yellow.

2. *Canarine, alizarin and flavopupurin, chrysomine, nitro-alizarin, alizarin brown, alizarin blue.*

Canarine: Caustic soda solution yellow; insoluble in sulphuric acid.

Alizarin: Caustic soda solution violet blue, changing to red on heating with powdered zinc.

Anthrapurpurin and flavopurpurin: Alkaline solutions fuchsine red.

Chrysamine: Alkaline solution orange, sulphuric, fuchsine red.

Nitroalizarin: Alkaline solution red. On being reduced by powdered zinc the colorless solution placed upon filter paper produces indigo blue stains.

Alizarin blue: Difficultly soluble in caustic soda to green solution which stains filter paper violet.

Alizarin brown: Alkaline solution olive brown, sulphuric, red brown.

3. *Indulines, nigrosine, rosaniline blues or diphenylamine in alcohol.*

Indulines and nigrosine: Alcoholic solutions greenish-blue. Benzine extract colored with very marked brown-red fluorescence.

Blues in alcohol: Alcoholic solutions deep blue, becoming

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green by the addition of hydrochloric acid. Benzine extract without dichroism.

4. *Indophenol:* Alcoholic solution blue, becoming brownish-red on the addition of hydrochloric acid.

5. *Magdala red:* Alcoholic solution bluish-red with cinnabar red fluorescence.

6. *Primrose, cyanosine.*

Primrose: Alcoholic solution bluish-red with yellow fluorescence.

Cyanosine: Alcoholic solution bluish-red with brick-red fluorescence.

7. *Indigo:* The finely pulverized product placed in ammonia in contact with powdered zinc is reduced, giving a solution which produces blue stains upon filter paper. I. A. P.

Analysis of Grease.—L. Archbutt, J. Soc. Chem. Ind. **7**, 494. In the analysis of dirty grease, grease for railway axles, etc., the author proceeds as follows:

Ten gms. of the sample are stirred in a beaker with ether until *thoroughly disintegrated.* The mixture is then rinsed into a separator and shaken repeatedly with quantities of 10 c. c. each of HCl (1.10) till all metals are removed. (Iron and aluminium can only be removed by *strong* acid. Ether dissolves ferric chloride from its aqueous and *dilute* acid solution.) The ethereal solution which remains is then washed three or four times with water in quantities of 10 c. c. each time.

Acid Extract.—Wash with ether to remove oil mechanically carried over and add the ether to the main quantity. Run the acid solution into a basin and let the ether spontaneously evaporate; then take to dryness, redissolve and estimate the *metals* in the usual manner.

The Ethereal Solution.—The free fatty acids are obtained by shaking with a mixture consisting of 10 c. c. 10 per cent. caustic soda solution, 5 c. c. methylated spirit and 35 c. c. water in a separator. The shaking is cautiously performed so as to avoid emulsifying and is continued ½ to 1 minute. The soda solution is drawn off into another separator after separa-

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tion has taken place and the ethereal solution is shaken with another 50 c. c. of the same soda solution and the soda added to the first portion, together with two or three aqueous washings of the ether. The mixed alkaline solution in the second separator is then shaken with ether to remove any traces of neutral oil and is then run into a third separator where the liquid is acidified with hydrochloric acid, the separated fatty acid extracted with ether, the ether evaporated and the fatty acid weighed.

The substance not removed from the ether by treatment with caustic soda is separated by evaporating the ether and is weighed. It is then saponified and extracted with ether. We have now two portions, an alkaline solution and an ethereal extract.

The Alkaline Solution.—Acidify and estimate fatty acids existing in the grease as neutral oil or fat. If the grease contained rosin, part of it (about 10 per cent.) will be found here; the rest of the rosin will be found as free fatty acid.

The Ethereal Extract.—Consists of *Hydrocarbon Oils*, *Cholesterin* and *Unsaponifiable Matters*, *Higher Alcohols*, etc.

The Action of Sulphur Chloride (S_2Cl_2) on Oils.—C. A. Fawsitt, J. Soc. Chem. Ind. **7**, 552. 30 gms. of oil were weighed in a small beaker which was placed in a larger beaker and the interval filled with cotton wool. From 2–5 c. c. S_2Cl_2 were then added with constant stirring and the rise in temperature and also the time interval required to reach the highest point attained noted.

The results are tabulated* and the rise in temperature with 2 c. c. chloride was with sperm 37°, seal 45, whale 57, neatsfoot 51, lard 40, rape 53, cotton seed 49, linseed 57, olive 52, castor 56, cod liver 55, mineral (sp. gr. .893 at 15) 25, palm 35, palm nut 5, rosin 31, oleic acid 53, stearic acid 5, glycerol 21.

In all cases except palm oil the resulting mass is thicker than the oil itself; with castor oil the action is so rapid that it is difficult to secure perfect mixture. In some cases an abund-

*For table see original paper.

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ant evolution of hydrochloric acid gas takes place (with linseed, castor, cod liver, mineral, palm, rosin, and oleic acid).

The author does not venture to propose this as a method for the detection of adulteration but states his observations as a contribution to the study of the subject.

AGRICULTURAL ANALYSIS.

EDITED BY H. W. WILEY.

MILK ANALYSIS.

Use of Asbestos Cloth Instead of Blotting Paper in the Adams Method.—Johnstone has reported to the Society of Public Analysts favorable results attending his experiments in substituting asbestos paper for blotting paper in the Adams method of fat estimation. (Analyst, Dec. 1887, p. 234.)

NOTE.—I called attention to the use of asbestos paper for this purpose two years ago, as will be seen on page 81, of Dept. of Agriculture Bulletin No. 13, part 1.

An Instrument for Calculating Milk Results.—Richmond has described an instrument for calculating milk analyses based on the relations existing between fat, solids not fat and specific gravity in milk as established by the paper of Hehner and Richmond published in the Analyst, vol. 13, p. 26. The instrument consists of a slide rule, on one side of which a scale of which one division equals one inch, represents total solids. The other scale, one division of which equals 1.164 inches represents the fat; while the scale representing specific gravity has a division equal to 1.254 inches.

The instrument is based upon the formula $T - .254\,G = 1.164\,F$. To use the instrument the lines indicating total solids and specific gravity found by analysis are placed together. The fat is then read off by an arrow on the other side. Where many analyses are to be made the instrument is especially valuable since it eliminates all chances of error in calculation. (Analyst, 1888, Vol. 13, No. 144, p. 65.)

Estimation of Fat in Milk and Cream.—Werner Schmid proposes the following method of estimating milk fat. A test

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tube of about 50 c. c. capacity is graduated in tenths of a cubic centimeter; 10 c. c. of milk or 5 c. c. of cream are placed in the tube, and 10 c. c. concentrated hydrochloric acid. The contents of the tube are boiled with constant shaking until the liquid is dark brown. After cooling in water add 30 c. c. ether, shake, allow to stand until the ether solution has separated, measure its volume and remove 10 c. c. with a pipette; place in a porcelain crucible, evaporate and dry at 100° in air bath. Calculate to total volume of the ether solution. The results are said to be exact. (Ztschr. anal. Chem., **27**, p. 464.)

The Relation of Specific Gravity, Fat and Solids not Fat in Milk.—Hehner and Richmond have made an exhaustive study of the relations existing between the specific gravity, fat, and solids not fat in milk. Three sets of determinations of the fat were made, viz: extraction from a paper coil, from plaster of Paris, and the direct extraction of the dried total solids. All previous formulæ relating to the above relations have been based upon imperfect methods of fat extraction. The work of Hehner and Richmond is therefore especially valuable on account of being based upon the Adams method of extraction. Forty-two analyses of various kinds of milk were made. For discussion of the formulæ the original paper is cited. The working formula obtained is $T - .254\ G = 1.164\ F$.

A table accompanying the paper gives the percentage of fat calculated for specific gravities ranging from 1024.0 to 1034.0 and for total solids, from 10 per cent. to 15 per cent. inclusive.

The author strongly recommends that no milk analyses be accepted as correct which do not correspond closely with the calculated results. (Analyst. Vol. 13, No. 142, p. 26.)

Sources of Error in Soxhlet's Method of Estimating Fat in Milk.—Weinwurm has determined the error which may arise by allowing the ether fat solution obtained by Soxhlet's method, to stand for varying lengths of time before its specific gravity is determined. As a result of his experiments it appears that the apparent percentage of fat is raised by allowing the solution to stand for a long time. For the first twenty-

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four hours, however, this increase is only small, the amount, at most, being a few hundredths of a per cent. By standing a long time the apparent percentage of fat gradually increases and appears to reach a maximum at the end of ten days. The amount of increase in that time may be .25 of one per cent. (Repertorium No. 19 of the Chemiker-Zeitung, 1888, p. 151, and M. Zg., 1888, 17, p. 401.)

Estimation of Dry Substance and Fat in Milk by Means of Wood Fibre.—Ganttner proposes the use of wood fiber for the estimation of fat in milk, which he uses as follows: 2 grams of wood fiber are dried at 105° to constant weight in a dish containing a small glass rod. The total weight of the dish, glass rod and fiber is noted. After weighing the dish, which is covered with a neat fitting cover to prevent the absorption of water, five to six grams of the milk are poured upon the wood fiber and the exact amount taken determined by reweighing the bottle. During evaporation the mass of fiber is pressed from time to time against the sides of the dish so that no particles thereof remain attached thereto. The final drying is made in an air bath, and the whole time required for the evaporation and drying should be about 2½ hours. From the increase in weight the amount of dry substance is determined. The mass of fiber is now transferred to a Soxhlet extraction apparatus and if necessary the dish rinsed with petroleum ether. The extraction of fat and the weighing thereof are carried on in the usual way. The author has also used this method for the determination of water in butter and other fats and oils. (Ztschr. anal. Chem., Vol. 26, No. 6, p. 678.)

The Chemical Action of Some Micro-Organisms in Milk.—Warington has studied the effect of certain micro-organisms on the curdling of milk. This curdling is effected either by the formation of a rennet like ferment or by the production of lactic acid. The amount of lactic acid required to curdle milk depends on the temperature, the amount growing less as the temperature rises. Five different organisms were examined

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which had the power of curdling milk but in very different degrees. They were Staphylococcus candidus, B. termo, M. gelatinosus, B. fluorescens liquescens and M. ureae.

Some of them readily curdled milk at a temperature as low as 10°. They do not at that temperature, however, produce an appreciable acidity. They therefore act plainly as a ferment. A large quantity of gas is evolved during the action of the same on milk.

Five organisms were also found to act as peptonizers; they are: B. subtilis, B. anthracis, B. floccus, B. toruliformis and Finkler's comma. The milk treated with these organisms at 22° becomes clear after a few days. The clear fluid is rich in pepton. A few organisms render milk after a time decidedly alkaline, two of these are, B. fluorescens non liquescens and the bacillus of septicaemia.

Cultivation in milk is an excellent method of distinguishing micro-organisms. (Chem. News, June 22, 1888.)

Reduction and Rotation Power of Milk Sugar.—Deniges and Bonnans have reviewed the literature concerning the reduction of copper solution by milk sugar. As compared with pure glucose the reducing power of lactose is as 96 to 136. The copper solution employed contained 34.65 grams of pure crystallized copper sulphate and 10 c. c. pure sulphuric acid per liter. The alkaline solution was composed of 250 c. c. of soda lye of 36° strength in which was dissolved 150 grams of crystallized rochelle salts; 10 c. c. of this solution was added to each 10 c. c. of the copper solution.

For the determination of the rotatory power of lactose the authors used a pure sugar obtained by three crystallizations. The specific reducing power for the anhydrous sugar at 20°, was 55.30 for concentration varying from 4 to 36 per cent. For the crystallized sugar the specific reducing power in the same condition is 52.53. The general formula for the crystallized salt would be $[a]=52.53+(20-T)\times.055$. The number .055 is the correction to be applied for each variation of 1° in temperature. The numbers obtained by the authors are

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exactly those given by Schmoger. (Journal de Pharmacie et de Chimie, April and May, 1888, pp. 363 and 411.)

Estimation of Sugar in Milk by the Polariscope.—Vieth discusses the method adopted by the Association of Official Agricultural Chemists for the estimation of sugar in milk which was originally described by me in the American Chemical Journal, Vol. 6, No. 5. The author is of the opinion that acetic acid and sub-acetate of lead can be used with equal advantage with mercuric nitrate and nitric acid for preparing the milk for polarization. He, however, prefers the use of the mercury salt. He calls attention to the correction which should be made in the reading of the polariscope for the volume of the precipitate. According to Veith this correction in the method adopted by the Association is too small. The volume of the precipitate is equal to the combined volumes of the precipitated casein and fat carried down with it. The method employed by Veith for making the correction for the volume of the precipitate is illustrated by the following example.

Given a milk with a specific gravity of 1.0325 which contains 3.72 of fat. Add to 50 c. c. of this milk 1½ c. c. of the mercuric nitrate solution. The polarization of the filtrate shows 5.1 milk sugar. The necessary calculations for the correction of this number are as follows:

93 : 100 : : 372 : x whence x = 4, the volume occu-occupied by the fat. 103.25 : 96 : : 51 : x whence x = 4.74. The number 96 in the above formula represents 100 c. c. of the liquid less 4 c. c. the volume of the fat. The number 4.74 represents the percentage of crystallized milk sugar. The percentage of the anhydrous milk sugar would therefore be 4.5. (Analyst, Vol. 13, No. 144, p. 63.)

Bicarbonate of Sodium in Milk.—Proust makes an energetic protest against the addition of bicarbonate of sodium to milk for the purpose of preserving it. His principal objection to the use of the above salt is based upon its action on lactic acid, the lactate of soda being a salt injurious to children. (Chem. Central-Blatt, No. 24, 1888, p. 837.)

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Determination of Milk Constituents.—R. Palm, Ztschr. anal. Chem., **26**, 319. Tannin precipitates all the albuminoids from milk, but the ratio of tannin to albuminoids in the precipitate is not constant. The tannin may all be washed out by alcohol, but in doing this albuminoids also dissolve slightly. The author finds that if a mixture of three parts ether and one part absolute alcohol be used for washing the precipitate the tannin may be washed out without loss of protein; or, the freshly precipitated proteintannate may be treated with excess of lead acetate solution and warmed to 30°–35°; the tannin then separates as lead tannate, while the proteine dissolves in the excess of lead acetate. The lead in the filtrate is then precipitated with sulphuretted hydrogen and the filtrate evaporated to dryness gives the albuminoids.

Mercuric nitrate may also be used as the precipitant provided the solution is kept neutral by the addition of caustic potash solution. If this is not done the acid set free dissolves some of the precipitate formed at first. It is best to have a slight excess of alkali at the end to prevent the occurrence of basic mercury salt. The precipitate may then be treated in either of two ways. 1. It is washed with alcohol, dried at 100° on a weighed filter and weighed. The filter and contents is then treated with aqua regia, the mercury precipitated as metal or as sulphide and after being calculated to oxide subtracted from the weight of the precipitate, or, 2. The fresh precipitate is heated with barium hydroxide solution which dissolves the albuminoids and precipitates mercuric oxide, the barium precipitated from the filtrate with sulphuric acid and the filtrate evaporated to dryness and weighed. The figures obtained for milk sugar are usually much too high, as the Fehlings solution used is acted upon by the lactopeptone hemialbumose and coloring matter left in solution when the albumen and casein are separated in the ordinary way. The author finds that the best method consists in evaporating the milk to dryness, extracting the fat with light petroleum, treating the residue with finely divided lead oxide and water (0.2 to 0.3 gms. PbO for 10 gms. milk) evaporating to dryness, treating

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with a little water and filtering through a weighed filter. The albuminoids with the lead oxide remain upon the filter while the milk sugar with a little dissolved lead oxide is found in the filtrate. After washing carefully, the residue is dried, weighed, and then burned with addition of nitric acid to convert the lead into oxide. The lead oxide is subtracted from the weight of the precipitate and the remainder is the protein present. The milk sugar is obtained by difference. The results obtained in this way are nearer the truth than those obtained by the use of Fehlings solution.

In the evaporation of milk the author has repeatedly noticed that the milk, at first alkaline, became acid from the formation of lactic acid. This shows that light petroleum should be used instead of ether for the extraction of the fat, since lactic acid is slightly soluble in ether. The lactic acid is removed with ether after the separation of the fat, the amount determined, calculated to milk sugar and the amount added to that of the milk sugar otherwise found. E. H.

Variations in the Composition of Milk.—Fleishman's formula for estimating the fat in milk by the relations existing between the specific gravity and total solid matter has been further tested by Harold Faber.

He finds the mean results about .2 per cent. too low. The solids in milk, after deducting the fat, are nearly constant, viz : 8.7 to 8.8 per cent.

The per centage of total solids was determined as follows : 10 grammes of the milk were dried for 5 hours on pumice stone at 89–100° and the loss of weight noted. The author has collected the analyses of 50000 samples of milk, 10000 of which were made by himself.

As a result of this extensive study the following facts appear :

1. The dry matter in milk, less the fat, is practically a constant quantity, viz : 8.75 per cent.

2. Evening milk contains more fat than morning milk.

3. In October and November milk is richer in fat than at any other season of the year. (Versuchs Stationen, May, 1888, p. 316.)

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Benzoic Acid in Milk.—F. M. Horn states that the milk offered for sale in Vienna often contains, as a preservative, benzoic acid. The quantitative estimation of the acid present is made as follows: 10–15 g. of the milk are diluted with the same quantity of water, warmed with HCl or $HC_2H_3O_2$ until coagulated. Boil, filter and wash with warm water. Evaporate the filtrate almost to dryness; treat with alcohol of 40–50 per cent., stirring with a glass rod; filter and wash well with dilute alcohol. Neutralize the filtrate exactly with NH_3, removing any excess by evaporation. If a precipitate be formed filter.

Add to the cooled filtrate an equal volume of absolute alcohol, and then drop by drop a solution of copper sulphate. A light blue precipitate of benzoate of copper is produced. This is either washed with alcohol and dried at 100°, or ignited and the metallic copper weighed. (Chem. Central-Blatt, 1888, No. 8, p. 260.)

BUTTER ANALYSIS.

Action of Alcohol on Butter Fat.—Cochran has made experiments on the solubilities of the different glycerides of butter in alcohol with reference to the quantity of volatile acid which the dissolved and undissolved portions would yield when treated by Reichert's method. As a result of the work it is seen that that portion of the glycerides dissolved by ethyl or methyl alcohol is richer in volatile acids than the undissolved portions. The iodine number of the dissolved fat is less than the undissolved fat. The melting points of the fats dissolved by alcohol is less than that of the undissolved fats.

The above facts would be of importance in the examination of butters to which it is suspected artificial butyrates may have been added. (Analyst, Vol. 13, p. 55.)

A Quick Method of Distinguishing Oleomargarine in Butter.—Dubernard has proposed the following method for a qualitative examination of butter for oleomargarine. The method rests upon the observation that pure butter vigorously shaken with ammonia at a temperature of from 70° to 80° and

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afterwards heated to 100° produces only a small amount of foam which does not last a long time. Margarine on the contrary, produces a large quantity of lasting foam. In order to distinguish butter from margarine by this method the following manipulation is pursued.

In a test tube place about three grams of the butter to be examined. Heat to 95° or 100° in a water bath and then allow to cool to about 80°. Add to the melted substance 5 c. c. of ammonia, shake vigorously and place again in the water bath and heat to 95° to 100°. The ammonia is volatilized with the formation of foam. The foam in the tube rises more or less according as the butter contains a larger or smaller quantity of oleomargarine. In mixtures of pure butter with known quantities of margarine the tube can be graduated and the relative quantities of butter and margarine thus approximately determined. (Chemiker-Zeitung, 1888, No. 46, p. 760.)

Detection of Adulterations in Butter.—Bockairy proposes the following method for the detection of adulterations in butter which rests upon the different solubilities of fats in toluene: Place in a test tube 15 c. c. of pure toluene, add 15 c. c. of the filtered fat and 40 c. c. of strong alcohol at 18°; the toluene holding in solution the fatty matter remains at the bottom of the tube. By means of a water bath the tube is heated to 50° and thoroughly shaken. If the sample is of butter fat, or a mixture of butter fat and some other kind there is no turbidity; but if no butter be present a turbidity is at once manifested. The tube is placed in water at a temperature of 40° for half an hour; pure butter gives no turbidity at the end of that time, but if other fats are present the mixture will appear turbid. (Chem. News, July 6, 1888, p. 11, and Bul. de la Societe Chimique de Paris, Vol. 49, No. 5, p. 331.)

Difference Between Natural and Artificial Butter.—C. J. VanLookeren proposes the following for a characteristic test between pure and falsified butter. A small amount of butter is melted in a teaspoon and a drop thereof placed in boiling

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water contained in a watch glass. If the butter be pure a thin film of fat is formed upon the hot water which breaks up into numerous fat globules which tend to collect quickly at the periphery. With oleomargarine, etc., a thin film of fat is formed in the same way, which, however, breaks up into only a few large drops which remain distributed over the whole surface of the water. The conditions for the success of the experiment are that the water be perfectly pure and clear and the melted butter-fat very hot. (Abstract in the Repertorium of the Chemiker-Zeitung, No. 18, 1888, p. 143, from Milchztg. 1888, 17, 362.)

A Modification of Koettstorfer's and Reichert's Processes.—Lowe has proposed the following method of determining the volatility and saponification equivalent of butter and other fats: About two grams of the filtered fat are saponified with 10 c. c. of normal alcoholic potash in a stoppered flask. The alcohol is then boiled off and the soap dissolved in 50 c. c. of hot water. The excess of potash is then determined with semi-normal sulphuric acid solution. The saponification numbers having thus been determined enough additional sulphuric acid is run in to make 25 c. c. in all. The flask is then connected to a condenser and 50 c. c. distilled off, filtered and determined in the usual way. The same flask is used throughout the whole process, one of 200 c. c. capacity answering very well. The whole process does not occupy more than two hours and can be completed often in less time.

Tyrer, criticising the process of Mr. Lowe was of the opinion that the quantity of fat taken, 2 grams, was too small since it gave only about one-tenth of a gram of volatile fatty acids. The alkali also dissolved some of the glass, thus introducing an error of which no account was taken. Carbonic acid moreever, expelled by this method, increased the apparent estimate of filtered fatty acids. (Jour. Soc. Chem. Ind., Mar. 1888, p. 185, May 1888, p. 376.)

Saponification Without the Use of Alcohol.—Mansfeld, in order to avoid the losses due to etherification, during saponi-

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fication in the presence of alcohol, has proposed to carry on the process of saponification preparatory to the estimation of volatile acids in butter without the use of alcohol. The method employed is as follows: Five grams of the melted and filtered butter fat are taken; into the melted fat are allowed to run 2 c. c. of a potash lye containing 100 grams caustic potash in 100 c. c. of water. The flask is closed with a stopper carrying a glass tube drawn out to a capillary point, the flask is then placed in an air bath heated to about 100° and allowed to remain for 2 hours. At the end of that time the saponification is completed. 100 c. c. of water are now added, the flask placed in a water bath until the soap is dissolved, which is decomposed and subjected to distillation in the usual way. (Chemisches Central-Blatt, June 23, 1888, p. 870, from M.Z. 17, 281–83.)

Wollny's Criticism of the Reichert-Meissl's Method.—The method of determining volatile fatty acids devised by Reichert has, during the past year, been subjected to an extended criticism by Dr. R. Wollny of Kiel. Dr. Wollny as a result of 98 analytical tests was convinced of the truth of the statement of Prof. Fresenius that the Reichert method was totally unreliable for the determination of very small quantities of butter in oleomargarine.

As a result of his analytical work Dr. Wollny was convinced that the chief source of error in the Reichert work was due to the absorption of carbonic acid. He asserts that the error which may arise from this source must amount to as much as 10 per cent. butter and renders the results obtained by the method quite inaccurate. It being very difficult to obtain an alkali free from carbonate the author decided to use a 50 per cent. solution of caustic soda instead of potash, since in a solution of that strength the chloride, nitrate, sulphate and carbonate of soda are quite insoluble. An arrangement was also devised by which the solution of caustic soda could be kept and drawn off for use without risk of absorption of carbonic acid. Such a solution made and kept in this way gave for 3 c. c. treated by the ordinary process of Reichert's distillation,

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an amount of volatile acid sufficient to neutralize from .2 to .3 c. c. of the decinormal barium hydrate solution. The author's precautions to prevent absorption of CO_2 are wholly unnecessary when the saponification is carried on in a closed flask.

Dr. Wollny further discusses the errors due to the formation of butyric ethers during saponification and distillation, and also the error due to the mechanical translation of particles of insoluble fatty acids during the process of distillation, and the error due to shape and size of the vessel in which the distillation is carried on and the time of its duration. The magnitude of these errors he states as follows:

(1) Due to absorption of carbonic acid, 10 per cent.

(2 and 3) Formation of butyric ether, 13 per cent.

(4) Cohesion of fatty acids, 30 per cent.

(5) Shape and size of vessel, 5 per cent.

M.Z. 1887, Nos. 32, 33, 34, 35, and the Analyst, 1887, Nos. 139, 140, 141, 142.

Dr. Wollny further describes the exact methods to be employed in the examination and the results obtained, for the details of which I refer to the original papers.

As president of the butter commission of the German Dairy Association Dr. Wollny has proposed the following method to be employed in the comparative examinations of butter for the forthcoming report of the commission, (see M.Z. No. 25, 1888.) In the preparation of the deci-normal barium solution each one of those taking part in the analyses has been furnished with samples of normal sulphuric acid, pure crystallized chloride of barium, and pure peroxalate of potash. In addition to this for testing the refractometer samples of olive oil, nitrobenzol and monobromnaphtalin have been sent. Following are the details given by Dr. Wollny for the preparation of the reagents and the conduct of the analysis.

METHOD PROPOSED BY DR. WOLLNY FOR THE EXAMINATION OF BUTTER FOR THE COMMISSION OF THE GERMAN DAIRY UNION. (From the Milch Zeitung, 1888, No. 25, et seq.)

1. *Proving the Weights and Burettes.*

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The weights which are to be used must be carefully compared and the burettes calibrated.

2. *Estimation of the Strength of Normal Sulphuric Acid.*

A clean dry dropping bottle of about 60 grams content, the tip of which is touched with vaseline on the outside, is carefully weighed. 35 or 40 grams of normal sulphuric acid are then placed in it and it is again weighed. Afterwards five portions in duplicate of about three grams are weighed in a beaker glass of 300 c. c. capacity. The drop bottle being weighed after each portion, the exact weight of the normal sulphuric acid in each portion is determined. 100 c. c. of recently boiled distilled water are added to each of the portions. 100 c. c. of this distilled water must not require more than two drops of barium solution to give color after 1 c. c. of the phenolphtalein solution has been added. The samples are heated in the water bath to the boiling point and to each portion so many c. c. of dilute barium chloride solution added that for each gram of the normal sulphuric acid there are present 10 c. c. of $BaCl_2$. The barium chloride solution contains 15 grams of the salt in one liter of distilled water. Afterwards the beakers are covered with watch glasses and allowed to stand for 15 minutes over the water bath. The precipitates are to be collected upon ash free filters of 9 cm. diameter and washed with hot distilled water until the chlorine reaction disappears. After drying and incineration the weight obtained is to be multiplied by the factor .34331. The five duplicate portions, after the addition of 1 c. c. of phenolphtalein solution, are treated with barium solution until the red color appears. The numbers obtained are to be calculated to 100 grams of the normal sulphuric acid.

3. *Estimation of Saturation of the Normal Sulphuric Acid by the Barium Solution.*

From the results obtained by the above analyses the exact strength of the deci-normal barium solution is to be determined.

4. *Titration of Barium Solution with Potassium Peroxalate.*

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One gram of the peroxalate of potassium, after drying for 12 hours in a desiccator over sulphuric acid, is placed in a weiging bottle similar to the one described above. 60 grams of hot distilled water are then added and after the salt has been dissolved and the solution cooled the weighing bottle is again weighed. About 12 grams of the solution are now run into each of five beaker glasses and the exact amount in each one determined by reweighing the weighing bottle. 90 c. c. of recently boiled distilled water are now added together with 1 c. c. of phenolphtalein solution. The barium solution is now added until the red color, which at first disappears, remains for at least five minutes. The results are calculated to the strength of the barium solution according to the formula,

$$T = \frac{10000 \times p\,(b-t)}{84.5\,n\,(l-t)} \text{ in which}$$

t=the weight of the weighing bottle empty.

b=the weight of the weighing bottle+the peroxalate.

l=the weight of the weighing bottle+the peroxalate solution.

p=the weight of the portion of the solution employed.

n=the number of c. c. of barium solution used.

5. *Estimation of the Volatile Acids after Saponification with the Aid of Alcohol.*

5 grams of the butter fat are weighed into an Erlenmeyer flask, 10 c. c. of alcohol at 96 per cent. and 2 c. c. of concentrated soda lye at 50 per cent., which has been preserved in an atmosphere free of carbonic acid, are added. The flask furnished with a reflux condenser, is heated with occasional shaking in a boiling water bath for ¼ of an hour. The alcohol is then distilled off by allowing the flask to remain for ¾ of an hour in a boiling water bath. 100 c. c. of recently boiled distilled water are then added and allowed to remain in the water bath until the soap is dissolved. The soap solution is then immediately decomposed with 40 c. c. of dilute sulphuric acid (25 c. c. sulphuric acid to 1 liter), and the flask

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immediately connected with the condenser. This connection is made by means of a 7 mm. diameter glass tube which 1 cm. above the cork is blown into a bulb 2 cm. in diameter, the glass tube is now carried obliquely upwards about 6 cm. and then bent obliquely downward; it is connected with the condenser by a not too short rubber tube. The flask is now warmed by a small flame until the insoluble acids are melted to a clear transparent liquid. The flame is now turned on with such strength that within half an hour exactly 110 c. c. are distilled off. 100 c. c. of the distillate are now filtered off, placed in a beaker glass, 1 c. c. of phenolphtalein solution added and titrated with barium solution; when the red color is shown the contents of the beaker glass are poured back into the measuring glass in which the 100 c. c. was measured, again poured back into the beaker and again titrated with the barium solution until the red color becomes permanent. The distillation should take place in as nearly 30 minutes as possible.

6. *Estimation of the Volatile Acids after Saponification without Alcohol.*

Five grams of the butter fat are saponified with 2 c. c. of concentrated potash lye preserved from contact with carbonic acid. The lye solution is made by dissolving 100 grams of the potash in 58 grams of water. By gentle rotation of the flask the lye and fat are intimately mixed together; the flask is then placed in a vertical position over a boiling water bath until the mixture becomes solid. It is then placed obliquely in the water bath. After it has remained here for two hours it is taken out and the remainder of the process continued as above.

7. *Estimation of the Mean Molecular Weight of the Volatile Fat Acids.*

The soap solution obtained by the titration of barium hydrate in number six is placed in a weighed platinum dish evaporated to dryness in the water bath, dried in a drying oven for two hours and again weighed.

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8. *Estimation of Volatile Fat Acids by Distillation from Magnesium Salts.*

Eight grams of butter fat are placed in an Erlenmeyer flask, treated with 3 c. c. of concentrated potash lye and 15 c. c. of alcohol as in number five and the alcohol then distilled off. The soap dissolved in 100 c. c. of water is washed with 250 c. c. of water in a measuring flask of 500 c. c. capacity and cooled to the temperature of the room. Then by means of a pipette, with constant shaking, 50 c. c. of magnesium sulphate solution, 15 per cent. strength are added, the flask filled up to the mark with water and vigorously shaken. The mixture is now placed upon an 18 cm. filter and 300 c. c. filtered into a measuring flask. The filtrate is brought into a flask holding about 500 c. c. which on the one side is joined with a steam generator and on the other with a condenser. Two c. c. of strong sulphuric acid together with two pieces of pumice stone are added. 250 to 275 c. c. are now distilled off into a measuring flask of 500 c. c. capacity, the distillate being filtered into the flask through a moistened filter. The gas flame under the distillation flask is then turned down low and the distillation continued in a current of steam until the 500 c. c. flask is full. After the filter which has been used has been washed with a little water the distillate is placed in a large flask of 1 liter capacity and 2 c. c. of phenolphtalein added and titrated.

9. *Estimation of the Volatile Fatty Acids from Copper Salts.*

The estimation is carried on exactly as in number 8 substituting 50 c. c. of copper sulphate solution for the 50 c. c. of magnesium salts. In the present case the distillate may be collected directly in the ½ liter flask without filtration since by precipitation with copper sulphate solution no insoluble fatty acids pass over during distillation.

10. *Estimation of Volatile Fatty Acids by Distillation in a Current of Steam According to Goldmann.*

5 grams of butter fat are weighed in a long-necked flask of about 300 c. c. capacity. 10 c. c. alcohol and 2 c. c. potash

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lye are added and the flask connected, on the one hand with a steam generator, and on the other with a condenser. The contents of the flask are now warmed with a small flame for 20 minutes, the condenser being directed obliquely downward and, in a measuring cylinder, 6 c. c. distilled off. The steam is then directed into the flask and 50 c. c. more collected. The soap is now decomposed with 5 c. c. sulphuric acid (20 c. c. strong acid diluted to 100 c. c.), the separated fat acids heated with a small flame until they form a clear solution and in a current of steam the volatile acids distilled off into a 500 c. c. flask. The size of the flame is so regulated that the contents of the distillation flask remain constant at about 30 to 40 c. c. and the distillation is continued until each succeeding 500 c. c. after the addition of 2 c. c. phenolphtalein solution, require not more than 2 c. c. of the deci-normal barium solution to produce the red color.

12. *Estimation of the Fatty Acids Soluble in 10 per cent. Alcohol: Roses Method.*

(a). 12.5 grams of butter fat are weighed into a graduated flask of 500 c. c. capacity, 50 c. c. of alcoholic potash lye (about 112 grams of potassium hydrate dissolved in absolute alcohol made up to 1 liter) are added and gently shaken. After five minutes as slight an excess of semi-normal sulphuric acid as possible is added. After two minutes dilute with water to 490 c. c. to destroy the foam, add 5 c. c. more absolute alcohol, fill up to the mark with water and then add as much more water as will correspond to the amount of fat taken. The flask is now shaken, contents filtered through a dry filter and 250 c. c. of the filtrate titrated with deci-normal potash lye.

(b). *Modification of the Above Process by Dr. Wollny.*—Weigh 6.25 grams of the fat in an Erlenmeyer flask of 300 c. c. capacity; add 25 c. c. of potash lye made with absolute alcohol as described above, and then dilute with absolute alcohol until not more than 74 c. c. and not less than 73 c. c. of semi-normal sulphuric acid are required to neutralize it. The flask is then closed with a stopper which carries a glass tube

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10 mm. wide and 50 cm. long; heat with a very small flame until the contents are near the boiling point, for about 20 minutes, until the smell of the butter ether has entirely disappeared. The flask is then cooled in water and 150 c. c. of recently boiled distilled water added. When the soap is dissolved and the whole mass cooled to about 15°, 75 c. c. semi-normal sulphuric acid are added. The flask is then closed with a rubber stopper and shaken vigorously for one minute. Filter through a strong dry folded filter into a graduated flask holding 200 c. c., pour the 200 c. c. into a large beaker glass and titrate with barium solution.

13. *Estimation of Insoluble Fat Acids.*

Treat 3 to 4 grams of the butter fat with 2 c. c. concentrated soda lye and 10 c. c. alcohol in a porcelain dish on the water bath and evaporate the soap to dryness. Dissolve the soap with 100 c. c. of hot water, add 5 c. c. concentrated sulphuric acid and heat the separated fatty acids for one hour on the water bath. Pour the contents of the dish on a filter of 11 cm. diameter, made of the best thick Swedish filter paper previously dried and weighed. Upon this filter the acids are washed with 1.5 liters of boiling water. The filter with the insoluble fatty acids, after they have solidified, is placed in a weighed beaker glass, dried for two hours in an air bath and weighed.

16. *Estimation of the Free Fat Acids.*

Ten grams of the butter fat are placed in a beaker glass with 2 c. c. of ether and 10 c. c. of alcohol and 1 c. c. phenolphtalein solution. The free acids are then titrated with decinormal alcoholic potash.

11, 14, 15, 17, 18, 19. *Combined Estimation of the Saponification Number, the Volatile, Soluble and Insoluble Fat Acids.*

(a). *Saponification Number.*—Five grams of the fat are weighed into an Erlenmeyer flask and 25 c. c. of alcoholic potash added. (25 c. c. alcoholic potash should saturate from 48 to 50 c. c. semi-normal sulphuric acid.) The mixture should be warmed as in No. 5, for a full hour with the reflux condenser.

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Meanwhile the same quantity of alcoholic potash should be exactly titrated with the semi-normal sulphuric acid and later being titrated by the barium solution used and the number obtained noted. The alcoholic soap solution is taken from the water bath, the solid parts adhering to the walls of the flask dissolved by gentle shaking, and, after the addition of 1 c. c. phenolphtalein solution, titrated with semi-normal sulphuric acid. The number obtained is subtracted from the number obtained in the blank experiment and calculated back to the corresponding number of c. c.'s barium solution.

(b). *Volatile Fat Acids.*—The alcohol is driven off from the exactly neutralized alcoholic soap solution obtained in the foregoing experiment and then an additional amount of sulphuric acid added amounting to 2 c. c. more than necessary to neutralize the original potash lye employed. The mixture is then diluted with 140 c. c. of recently boiled distilled water and two pieces of pumice stone added and, as in number 5, 110 c. c. distilled off, of which 100 c. c. after filtration is titrated.

(c). *Soluble Fat Acids.* After the end of the foregoing experiment the distillation flask is removed from the distillation tube and replaced by filling with distilled water, and placed as a receptacle under the condenser. The condensation water is now allowed to flow from the condenser and the condensed insoluble fatty acids driven over into the distillation flask by a current of steam. In like manner the insoluble acids collected upon the filter are washed into the original distillation flask. After the fatty acids are solidified the whole of them are brought into a cylinder 3.5 cm. wide and 15 cm. long which ends in a 6 cm. wide tube carrying a goose necked glass tube from its side, and on the lower end is closed with a rubber tube and pinch cock. The lower contraction of the cylinder is stopped with a plug of glass wool which forms a thick filter but allows hot water to run through easily. Under the goose neck of this wash vessel, which is held in a vertical position by a retort holder, is placed a graduated flask of 50 c. c. capacity into which the excess of water flows. When

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the acids have been brought from the distillation flask together with the pieces of pumice stone, into the wash flask any residue is washed out with the washing bottle with boiling water. The above must be so conducted that no drops of the fatty acid passes through the glass wool and that no fatty acid remains on the upper walls of the washing flask. The washing flask is furnished with a gum stopper carrying two holes. Through the one passes a tube for the inlet of steam, through the other a tube at least 8 mm. in diameter, cut off obliquely at the lower end and divided above the stopper into two branches; by means of one of these branches it is connected with a perpendicular condenser at least 8 mm. wide and through the other it is connected by means of rubber tube and pinch-cock with a hot water reservoir by means of a *U* tube reaching to the bottom thereof. Through the steam tube, which is somewhat bent at the end so that the steam is directed obliquely downwards and outwards against the sides of the washing bottle, a current of steam is conducted which stirs up in a lively manner the surface of the fatty acids which swim upon the top of the water, while the condensed water drops back out of the reflux condenser in a boiling hot condition and the excess flows through the goose neck into the measuring flask. The wash water collected in the 500 c. c. flask is titrated with barium solution with the addition of 2 c. c. phenolphtalein solution. This operation is repeated three times; in all 1.5 liters of wash water being collected. The total amount of barium solution required in the three operations is collected in one number.

(d). *Insoluble Fatty Acids.*—After the end of the foregoing experiment the wash flask is cooled until the fatty acids are solidified. The pinch cock closing the lower opening of the wash flask is opened, the water allowed to flow off and a current of air passed through the apparatus by means of an aspirator after the opening of the goose neck is lightly stoppered and the steam generator removed. The wash flask, together with the fatty acids and the glass wool plug, are completely dried in this manner, after at most, half an hour. The steam

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generator is now replaced with a flask which contains ether, free of water, alcohol and acids. The ether is brought to the boiling point by means of warm water and its vapor condensing in the washing flask dissolves the fatty acids and carries them into the weighed flask, of about 100 c. c. capacity placed below to receive them. When about 40 or 50 c. c. of ether have distilled over the operation is broken the outer end of the wash flask washed with ether and the weighed flask below is placed in a warm place in order to drive off the ether. The weighed flask containing the acids is now warmed in the water bath and placed under the receiver of an air pump. After the acids are completely freed from ether by this method the flask is again weighed and the weight of the acids noted.

(e). *Mean Molecular Weight of the Insoluble Fat Acids.*—The fatty acids obtained in the foregoing experiment are melted at a low temperature and from .8 to 1 gram weighed in a beaker glass, dissolved in 50 c. c. of alcohol, 1 c. c. phenolphtalein solution added and titrated with barium solution.

20. *Determination of the Iodine Number.*

Weigh out from .8 to 1 gram butter fat in a flask of about 200 c. c. capacity furnished with a glass stopper; dissolve in 10 c. c. chloroform and add 20 c. c. iodine solution. In case the liquid is not clear more chloroform must be added. If the iodine color should rapidly disappear add from 5 to 10 c. c. more. The amount of iodine added should be sufficient to secure strong coloration after standing 2 hours. Add 10 to 15 c. c. iodide of potassium mixture and 150 c. c. of water; titrate with thiosulphate of sodium solution until the iodine has almost disappeared. Add then a little starch solution and continue titration until the blue color has disappeared.

21. *Estimation of Refractive Index.*

Set the large Abbe refractometer with water at 18° so that the index reads 1.3330. The instrument should then be placed in a room which is kept at a temperature of about 25°. The estimation of the refractive index of butter fats cannot be made below 25° on account of the solidification of the fat.

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The instrument is also to be tested to 20° with olive oil, nitrobenzol and monobromnaphtalin.

25. *Determination of the Specific Gravity at Zero or 15°.*

A platinum crucible is supplied with a platinum wire handle so that it can be suspended from the hook of the balance. It is then weighed empty and afterwards its specific gravity taken in water at zero. The water is kept at zero by being placed in a small beaker glass, which in turn is put in a larger beaker closed and surrounded with finely pounded ice. The crucible is then dried and 15 grams of melted butter fat placed therein. The butter fat is allowed to solidify slowly at a temperature not below 15°. The crucible and its contents are then weighed in the air and placed in distilled ice-cold water for an hour. The whole is then weighed in water at zero as before. From these results the specific gravity of the fat at zero is determined. In the same way the specific gravity at 15°.

26. *Estimation of the Specific Gravity in Boiling Water by Means of the Pyknometer.*

A small flask of 50 grams, the neck of which is drawn out to a narrow tube and marked at the narrow place, is weighed empty. It is then filled with distilled water to the mark and placed for an hour in finely pounded ice. The contraction of the water is restored by the addition of ice-cold water until the mark is reached ; it is then dried, allowed to come to the temperature of the room and weighed. The same flask is then filled to the mark with boiling water and after coming to the temperature of the room weighed. The flask is then emptied, dried, filled with melted butter fat, kept in a boiling water bath for an hour, the butter fat filling to the mark, afterward cooled in the temperature of the room and weighed.

27. *Estimation of the Specific Gravity with Mohr's balance.*

This is determined in the usual manner by the use of a specific gravity bob the thermometer of which is arranged so as to show a temperature of 100°.

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28. *Estimation of the Specific Gravity with the Areometer in Boiling Water.*

This is determined by means of spindles furnished by the firm of G. C. Gerhard in Bonn. These spindles are graduated especially for specific gravity at a temperature of 100°.

29. *Estimation of the Melting Point.*

This is determined in straight or U-formed capillary tubes. They are filled with butter fat at 100° and placed in ice water for a quarter of an hour. The capillary tube is then placed with a thermometer in a beaker glass with water at 20° and slowly warmed with a small flame.

30. *Estimation of the Solidifying Point.*

Place about 100 c. c. of the melted fat in a test tube at 40°. Stir with a thermometer until the fat begins to solidify, the test tube meanwhile being placed in a large vessel containing water at 20°. The temperature will rise slightly when the solidification begins and the highest point reached is entered as the solidification point.

NOTE.—Dr. Wollny has proposed in the above scheme an exhaustive study of butter fat. Many points appear to be superfluous and others elaborated into unnecessary detail. The method of determining insoluble fatty acids appears to be more objectionable than any other part of the scheme. The method of making the melting point first described in the Journal of Analytical Chemistry (Vol. I, No. 1, p. 39) appears to have escaped the notice of the German commission. I also note with regret the apparent ignorance of the existence of the Gooch crucible existing in Germany.

Points to be especially commended in these investigations are sending samples and standard reagents, blanks for entering the analytical results and minute printed directions for conducting the manipulation.

The numbers prefixed to the several paragraphs correspond to the number of the column in the blank in which the results are to be entered. H. W. W.

Criticism of Wollny's Methods.—Goldmann criticises Wollny's original method chiefly because it gives only a part of the volatile acid present and takes no account of the whole. It has never been claimed, however, for the Reichert process that it gave anything more than a portion of the volatile acid present, but the percentage of the total volatile acids obtained is approximately constant and therefore the results are comparable among themselves.

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Goldman proposes to remove the last traces of alcohol after saponification by distillation in a current of steam. Before the distillation of any part of the alcohol, however, the solution is heated with a reflux condenser for half an hour so that any ethers which have been formed may be recombined by the excess of alkali present. The apparatus for the removal of the last traces of alcohol is illustrated in No. 14 of the Chemiker-Zeitung for 1888, p. 216.

Goldmann's paper is so long that for all details I can only refer to the original. The method finally adopted by him is as follows: Five grams of the melted butter fat are weighed in a flask of 300 c. c. capacity, the neck of which is 12 cm. long and 2 cm. wide. Add 10 c. c. alcohol 96 per cent. and 2 c. c. of a 50 per cent. aqueous soda lye, made and preserved out of contact with carbonic acid. The flask, furnished with a reflux condenser, is heated for twenty minutes with a small flame. The condenser is turned to an angle of 55° and 6 c. c. of the alcohol distilled off. The flame is then extinguished, the apparatus connected with the flask delivering steam and the whole of the alcohol driven off by a slow current of steam.

Full directions for the conduct of this part of the work are given by Goldmann.

After the alcohol is driven off the soap is decomposed by the addition of 5 c. c. of sulphuric acid containing 200 c. c. of strong acid to the liter. The volatile acids are distilled off in a current of steam and 600 c. c. of distillate taken which is titrated with one-tenth normal solution of barium hydrate. (Chemiker-Zeitung 1888, No. 12, p. 183, No. 14, p. 216, No. 20, p. 317.)

Application of the Reichert-Meissl-Wollny Method to Italian Butters.—Besana has made an extended examination of 114 samples of butter and from the study of them draws the following conclusions:

114 samples of butter examined belong to 30 provinces. These show a melting point from a minimum of 35° C to a maximum of 37° .7, not including one sample which seems to

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be essentially different in constitution. No positive relation has been established between the point of fusion and the quantity of volatile acids, therefore, the knowledge of the first offers no special utility.

The per cent. of volatile acids, or the quantity of the same expressed in c. c. of deci-normal alkaline solutions, shows a variation from a minimum of 21.83 to a maximum of 30.19. The classification of the 114 samples of butter according to their quality or condition would be as follows:

Volatile	acids	from	29 to 30.19	23	Samples.
"	"	"	28 " 29	25	"
"	"	"	27 " 28	49	"
"	"	"	26 " 27	9	"
"	"	"	25 " 26	3	"
"	"	"	24 " 25	2	"
"	"	"	23 " 24	1	"
"	"	"	21.80 22	2	"
				114	"

The variation in the quantity of the volatile acids, in the different butters, already recognized by various experimenters in Germany and Sweden, is confirmed by these researches also in the Italian butters. Even the butters of the same dairy may present quite different qualities, although made within a very few days of each other. Upon the cause of this variability I have not ventured, up to the present time, to present any theory, and I have not even sufficient data for the support or contradiction of the theories of others. I hold the causes to be biological, and I would like the researches tending to their discovery to be made by following very closely the chemistry of nutrition and of the lacteal secretions or the transformation of aliment into milk, keeping note of the quantity and quality of the food, the stage of lactation, the condition of health in the animal, etc.; but such researches, in my opinion, should be followed upon individual cases instead of upon a group of milch cows. (Prof. Carlo Basana, extract from the Journal "Le Stazioni Sperimentali Agrarie Italiane," 1888, Vol. XIV.)

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Modification of Bechi's Test.—The Italian Commission appointed to examine Bechi's test for cotton seed oil, recommend the use of some free nitric acid in the silver solution.

Solution No. 1 consists of—

$Ag\,NO_3$	1 gramme.
Alcohol	200 grammes.
Ether	40 "
$H\,NO_3$	0.1 "

Solution No. 2 is composed of—

Amyl alcohol	100 grammes.
Rape seed oil	15 "

An addition of 15 per cent. of cotton seed oil can be easily detected. With only 10 per cent. the determination is more difficult.

With too little free nitric acid pure olive oil may show a brown color, while too much will influence the color with cotton seed oil. In all cases the oils to be examined should be filtered.

10 c. c. of the oil, 1 c. c. of the silver solution and 10 c. c. of solution No. 2 are to be used in each test. (Chem. Zeit. 11, p. 1328.)

The Analysis of Butter.—V. Planchon, Mon. Scien., Sep. 1888. The author's experiments have shown that in the ordinary methods of butter analysis there are two serious sources of error. In the first place in melting and filtering a specimen of butter, as ordinarily done before saponification, decomposition takes place to a certain extent, resulting in an increase of soluble fatty acids. Again, in drying the insoluble fatty acids before the final weighing there is danger of loss by the escape of the volatile acids which remain even after perfect washing. In the case of pure butter this loss is sometimes quite high, while in oleomargarine it is scarcely appreciable. The greatest care is therefore necessary in the preliminary heating and final drying in order to obtain good results.

The author's method is based upon the following principle: If a given weight of fatty matter be saponified by a known

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quantity of alkali in excess and then the liquid rendered neutral by standard acid the quantity of alkali combined with the fatty acids can be determined. This will be in proportion to the glycerine originally combined with the fatty acids and displaced by the alkali. If now the addition of standard acid be continued until an amount exactly equivalent to the total amount of alkali used has been added the saponified fats will be decomposed, the separated fatty acids will rise to the top, the excess of alkali will be neutralized, and the filtered liquid will be acid or neutral according to the presence or absence of soluble fatty acids. If present, the amount is determined by standard alkali. The insoluble fatty acids are collected, dried until the loss becomes constant and then weighed. The solutions necessary for the analysis are, half normal sulphuric acid, normal alcoholic caustic soda solution and fifth normal aqueous caustic soda solution, all very exactly standardized. The paper contains the details of the author's method and a number of results showing its utility. I. A. P.

Influence of Alcohol on the Amount of Starch Obtained by Asboth's Method.—Seyfert discusses Asboth's method and Monheim's* paper with especial reference to the admixture of alcohol in the liquid from which the starch is precipitated by barium hydrate. By changing the quantity of alcohol added the per cent. of starch found in the same same sample of dried potato meal varied from 71.92 to 88.69 per cent. Eight other sets of analyses showed equally as great variations.

With pure starch pastes the same differences were established. According to the strength of the alcohol used in the analyses of a given substance entirely different per cent. of starch can be obtained. This is due to a portion of its barium hydrate being carried down in the precipitate. Changes of temperature were found often to produce a precipitation of barium hydrate in the bottles and burettes containing it. It is very difficult even perhaps impossible to fix the limits of the addition of alcohol so as to permit the complete precipitation of the

*This Journal II, 207.

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starch and prevent the precipitation of anything else. (Zeit. f. angewandte Chemie, 1888, No. 5, p. 126.)

NOTE.—In my laboratory the method of Asboth has proved to be unreliable.
H. W. W.

Behavior of Starch with the Alkaline Earths.—Lintner in investigating Asboth's method of starch determination was led to study the behavior of starch with earths allied to baryta. The results of his studies are summed up as follows :

1. Solutions of lime saccharate precipitate from weak starch solutions all the starch in combination with lime. Dextrine is not precipitated in like conditions.

2. One part of starch may unite with different quantities of lime in proportion as the latter is more abundant. The maximum seems to be one part of starch to .3164 part lime and the minimum .0952 part of lime, corresponding to the symbols $C_6H_{10}O_5CaO$ and $(C_6H_{10}O_5)_4$ CaO.

3. Barium hydrate acts with starch in a manner similar to sugar-lime solution. The mimimum and maximum compounds are $(C_6H_{10}O_5)_2$ BaO and $(C_6H_{10}O_5)_3$ BaO.

4. In presence of a small amount of alcohol the dextrines also give precipitates with BaO_2H_2.

5. Hydrate of strontium and strontium saccharate solutions do not precipitate starch completely. In the presence of alcohol however complete precipitation may take place.

6. The hydrates of the alkaline earths can not be used for the direct estimation of starch with satisfactory results. (Zeit. f. angew. Chem. 1888, No. 8, p. 232.)

Methods of Estimating Starch.—Winton has made comparative determinations of starch by—

1. Märcker's old process.
2. The same without use of basic lead acetate.
3. Märcker's new process.
4. Chittenden's method.
5. Sachse's method.

A pure starch made from potatoes was used, previously dried at 120° in hydrogen.

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The starch by difference in the above was 84.19 per cent. By determination the following numbers were obtained:

By method 1	84.63	per cent.
" 3	84.66	"
" 4	84.65	"
" 5	84.63	"

The starch in dried potato meal was also determined in triplicate with the following results:

	I.	*II.*	*III.*
By method 1	67.05	66.52	66.78
" 2	68.60	67.98	68.29
" 3	69.78	69.30	69.54
" 4	69.30	68.76	69.03
" 5	71.60	71.64	71.62

Asboth's method gave uniformly results, which were too low. The author concludes that the direct saccharification according to Sachse's method is the best and simplest, and that previous removal of the cellulose is not necessary. (Zeit. f. angew. Chem., 1888, No. 9, p. 273.

Estimation of Starch.—Asboth has replied to the various criticisms which have been made of his proposed method of estimating starch by precipitation with solution of barium hydrate.

After a brief statement of the views of his critics and a statement of results of comparative determinations of pure starch by his and other methods, Asboth says:

"As the analyses show, the results of the last two methods (Asboth's and Lintner's) agree tolerably well together. Whether with cereals I can obtain like results my later comparative experiments will determine."

"I have said in my first paper that those methods of starch estimation which rest upon inversion cannot give satisfactory results. In how far this statement should be modified in respect of Lintner's process my further experiments will determine." (Chem. Zeit. 1888, No. 42, pp. 693–4.)

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Detection of Flour Added to Chocolate.—5 g of the chocolate are weighed out in duplicate and treated in a 250 c. c. flask, the one with 100 c. c. boiling water and the other with 100 c. c. water at 35–40° for half an hour. The starch in the one case is in the paste form and in the other undissolved. Both samples are now tested for starch by the method of Asboth. 50 c. c. of the BaO_2H_2 solution are added to each flask, well shaken and made up to the mark with 45 per cent. alcohol. After bottling 50 c. c. of the clear liquid are titrated with $\frac{1}{10}$ N acid. The strength of the Ba solution is fixed in a similar manner. The number of c. c. used in the test is subtracted from the normal number and multiplied by 5. The difference (D) between the numbers obtained in the two samples represents the starch. The quantity of flour added is then determined by the following equations:

$$X = 10\frac{D - 1.25}{3}.$$

In a similar way the adulteration of other substances by flour can be detected and the extent of the adulteration determined. (Mansfield, Chem. Central–Blatt, 1888, No. 8, p. 259.)

NOTE.—The method of Asboth has been shown to be unreliable. In the present case, however, since all the samples are treated in the same way and the barium solution standardized in a solution containing the same quantity of alcohol as in its samples to be titrated the results may be approximately correct.

Alumina in Flour.—A wheat flour of best variety afforded .0075 g, phosphate of alumina per 100 g. flour.

The flour contained 8 per cent. gluten. 20 g. of the gluten prepared as carefully as possible, yielded .0185 g. aluminum phosphate. This gluten represented 250 g. flour, which would have contained according to the above analysis .0187 g. of the phosphate. Hence it appears that the whole of the alumina naturally contained in flour, is found in the gluten. (W. C. Young, Analyst, Vol. 3. Chem. Central-Blatt, 1888. No. 8, p. 259.)

NOTE.—The addition of alumina to flour in the form of baking powders and otherwise emphasizes the importance of knowing the mean natural content o alumina in flour.

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Adulteration of Flour.—The addition of 1–3 per cent. of potash or ammonia alum is said by P. Claes to be commonly practiced. C. proposes to distinguish this adulteration by using tincture of campeche wood. This strikes a blue color with alum. The tincture is prepared by digesting 3 g. of the wood cut into small pieces with 50 c. c. 90 per cent. alcohol for an hour cold. In a test tube holding about 35 c. c., put about 3 c. c. water and 2 g. of the suspected flour, and shake thoroughly. Add 1 c. c. of the tincture and fill the tube with a saturated common salt solution, without shaking. The color is compared with that produced in a similar way by adding 1, 2, 3 or 4 per cent. alum to pure flour. (Journal de Pharm, et de Chim., Vol. 17, p. 33, and Chem. Central-Blatt, 1888, No. 8, p. 260.)

NOTES.

—At the Cleveland meeting of The American Association for the Advancement of Science, Dr. F. A. Genth of Philadelphia was elected an Honorary Fellow. This is a great honor and we believe well deserved. At present the Association has the name of but one living Honorary Fellow upon its roll, that of Chevreul, the centenarian.

—Dr. F. A. Genth was, on June 19, removed from the chair of Chemistry of the University of Pennsylvania, by a vote of the Board of Trustees. Dr. Genth had declined to resign, and in answer to a request for his resignation wrote a letter to the Board which he has now published in pamphlet form.

—The aged scientist, Chevreul, attains his one hundred and second birthday to-day, thus beating Sir Moses Montefiore's record. But he is not expected to live through the Winter, as his strength is failing. So he spends most of the time in bed, though he still has a short daily drive. A deputation of Paris students who went to his house to-day to offer congratulations were not allowed to see him. They were received by

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his son, a promising young man of 79.—*London Correspondence N. Y. Times, Aug. 29.*

—Dr. Edgar F. Smith has been appointed Professor of Analytical Chemistry at the University of Pennsylvania.

—A complimentary dinner was given to Prof. Schorlemmer on May 25 to celebrate the conferring upon him of the degree of LL. D. by Glasgow University. A large number of English chemists were present, including many of Schorlemmer's former pupils.

—We have received from E. H. Sargent & Co. samples of Munktells Swedish Filter Paper sold by that firm. The first quality, No. 0, is now washed with hydrochloric acid and sold either in sheets or cut into round filters. The ash of the 9 cm. filters weighs

No. 0	. . . . .	0.00029 9ms.
" 1 F	. . . . .	.00142 "
" 2	. . . . .	.00095 "

The catalogued price of these filters is much less than for the corresponding sizes of Schleicher and Schüll's filters washed with hydrochloric and hydrofluoric acids.

—F. Seyfert finds that starch iodide contains 18.50 per cent. iodine and gives to it the formula $(C_{24}H_{40}G_{20})_6I_7$* (See Ztschr. angew. Chem. 1888, 15.) This substance has also been studied by H. B. Stocks (Chem. News **56**, 212; **57**, 183) to whose papers we must refer the reader.

OBITUARY.—On Thursday, August 30, J. Peter Griess at Bournemouth, England. Griess was well known as the discoverer and investigator of the Diazo-compounds. From 1859 to the time of his death he was scientific adviser to the firm of Allsopp & Son.

—Norman J. Fake, a chemist of the Department of Agriculture in Washington, was drowned in the Potomac while bathing on August 11. Mr. Fake although not quite twenty years of age had already gained distinction as a sugar analyst and was to have had charge of a part of the work of the Department during the present year. H. W. W.

*See this Journal I, 360.

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NEW BOOKS.

STAMMERS CHEMICAL PROBLEMS, with Explanations and Answers. Translated by W. S. Hoskinson. P. Blakiston & Co., 12 mo. cloth, 111 pages, 75 cts. This is a book which commends itself to all teachers of chemistry. The problems are well selected and are sufficient iu number. The book is well printed on good paper. E. H.

THE CONSTANTS OF NATURE. PART I.—New edition, revised and enlarged. By F. W. Clarke, Chief Chemist U. S. Geol. Survey, 8vo., 409 pp. Washington. Published by the Smithsonian Institution. This first part includes the specific gravity tables of the first edition, with additions and corrections. The list of organic compounds especially has been much enlarged, extending through 210 pages. Those who have used the first edition will appreciate Prof. Clarke's work in completing to date this useful compilation.

DISEASES OF THE LIVER—By Prof. DuJardin Beaumetz, translated by E. P. Hind, M. D. Published by G. S. Davis, Detroit, 1888, Paper, 25 cts. This little book by Dr. DuJardin Beaumetz is a very readable work. The matter is treated in the lively style peculiar to French authors. The vegetable medicaiments which we believe to act upon the liver are baptisin, ipecacuanha, euonymin, hydrastin, iridin, juglandin, leptandrin, phytolaccin, and the well-known ones of podophyllin, aloes, rhubarb and senna. He states that the maximum effect of podothylin is characterized by the curious fact that a maximum action on the liver is produced by moderate doses and not by large ones. This brochure systematizes our actual knowlege of the therapeutics applied to the liver and should be read by all thinking medical men. I. O.

BOOKS AND PAMPHLETS RECEIVED.—LeStazioni Sperimentali Agrarie Italiane, Vols. 14 and 15; Comparative Chemistry of Higher and Lower Plants. By Helen C. DeS. Abbott; University Studies, Vol. 1, No. 1. July, 1888, Lincoln, Neb.; Notes on the Literature of Explosives, XVII. By Charles E. Munroe; Mass. Agrl. Exp. Sta. Bulletins 30 and 31 and Analyses of Commercial Fertilizers, August and November, 1888; Kentucky Agr. Exp. Sta. Bulletins 14 and 15; Missouri Agrl. Exp. Sta., Bulletins 2 and 3; Ill. Agr. Exp. Sta. Bulletin No. 2; Conn. Agrl. Exp. Sta. Bulletin 95; Baton Rouge, La., Agrl. Exp. Sta. Bulletins 13 and 17; Fifth Annual Report of the Agricultural Experiment Station of the University of Wisconsin, Madison, 1888; Second Biennial Report of the Minnesota State Dairy Commissioner, St. Paul, 1889.

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Vol. II. October, 1888. Part 4.

THE

Journal of Analytical Chemistry

Edited by EDWARD HART, Ph. D.
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EASTON, PA.
PUBLISHED BY THE EDITORS.

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